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CONTROL OF VOLATILE ORGANIC EMISSIONS FROM EXISTING STATIONARY SOURCES

VOLUME I. CONTROL METHODS FOR SURFACE-COATING OPERATIONS

ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA

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CONTROL OF VOLATILE ORGANIC EMISSIONS FROM EXISTING STATIONARY SOURCES - VOLUME I: CONTROL METHODS FOR SURFACE-COATING OPERATIONS

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

Available methods which can be used to control the emission of organic vapors from surface coating operations are described. The methods consist of two types: (1) add-on control equipment, and (2) process and material changes. Available add-on equipment includes direct-flame incinerators, catalytic incinerators, and activated carbon adsorbers. Process and material changes which reduce or eliminate the use of organic solvents include (a) water-borne coatings, (b) high solids coatings, (c) powder coatings, (d) hot melt formulations, (e) electrostatic spraying, (f) electron beam curing, (g) ultraviolet curing. Graphs are given to determine the cost of incinerators at varying volumes and variation in inlet temperature, vapor concentration, degree of heat recovery, fuel costs, and hours of operation. Graphs are given to determine the cost of carbon adsorbers under varying volumes and vapor concentration. The available methods of measuring volatile organic emissions are discussed.

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Emission Standards and Engineering Division
Chemical and Petroleum Branch

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

November 1976

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Publication No. EPA-450/2-76-028

NOTICE

Volume I is the first of a continuing series of reports designed to assist the State and Regional Offices develop regulations for industries that emit volatile organics. It contains information on control schemes now being used, estimates of the cost of several systems and provides guidance for sampling and analyzing organic emissions.

We expect Volume II to be issued by the year's end. It will contain detailed information on alternatives available for reducing emissions from five coating industries; can, coil, fabric, paper and automobile. (Preprints of the sections for the first four are available now). Future volumes will provide guidance on the control of organic emissions from other industries. These should be especially helpful as revisions are made to future State Implementation Plans.

All questions concerning this series should be directed to John Haines, Assistant to the Director, Emission Standards and Engineering Division, FTS 629-5271.

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GLOSSARY

acfm	actual cubic feet per minute
Btu	British thermal units
cm^3	cubic centimeters
CH_4	methane
CO_2	carbon dioxide
CO	carbon monoxide
EPA	U.S. Environmental Protection Agency
°F	degrees Farenheit
FID	flame ionization detector
ft^3	cubic feet
g	grams
gal	gallon
GC	gas chromotography
H_2	hydrogen
hr	hour
in.	inch
kW	kilowatt
lb	pound
LEL	lower explosive limit
max.	maximum
min	minute
mg	milligram
mnHg	millimeters of mercury
MS	mass spectrometry
NAAQS	national ambient air quality standards
NDIR	nondispersive infrared absorber
NEDS	National Emissions Data System
NO_x	nitrogen oxides
O_2	oxygen
ppm	parts per million

scfm	standard cubic feet per minute
TRC	The Research Corporation of New England
(TM)	registered trademark
wt	weight
yr	year

1.0 INTRODUCTION

1.1 Purpose of This Series of Documents

Photochemical oxidant control strategies currently rely heavily on the substitution of organic solvents that are considered to be of relatively low photochemical reactivity, coupled with add-on control and process and material changes to reduce emissions of the compounds of higher reactivity. Recent information indicates that solvent substitution is of only marginal effectiveness in lowering ambient oxidant levels. This series of documents provides guidance on ways to reduce volatile organic emissions irrespective of photochemical reactivity. Specific source categories and available control technology for these sources are discussed in Volume II. Subsequent volumes will cover additional source categories.

1.2 Volatile Organic Sources

Volatile organics are emitted from a variety of anthropogenic sources. Total nationwide emissions for 1975 were estimated by EPA to be about 31 million tons, of which 19 million tons were from stationary sources. Evaporation of organic solvents contributed about 44 percent of the total from stationary sources; the remainder is from petroleum refining and distribution, industrial processes, and combustion of fuels and wastes.

Major industrial sources of volatile organics discussed in Volume II include automobile and light-duty truck assembly, can coating, coil coating, fabric coating, and paper coating. Other industrial categories which may be examined in future volumes are wood furniture manufacturing, degreasing operations, drycleaning, graphic arts production, tire manufacturing, petroleum refining, magnetic tape coating, miscellaneous printing and coating, metallurgical processing, production and use of synthetic organics such as plastics, rubbers and resins; production of various high-volume organic chemicals, pharmaceutical production, stationary combustion sources, and food processing.

1.3 Control Technology

Emissions of organic air pollutants can be reduced by (1) add-on control devices that either destroy or collect the organic for reuse or disposal and (2) process or material changes that reduce or eliminate the use of organics.

Today, the principal add-on control devices for the control of volatile organics are:

- Catalytic and noncatalytic (thermal) incinerators
- Activated carbon and other types of adsorbers
- Liquid scrubbers or adsorbers
- Condensers that use refrigeration or compression

Incineration is the technique most universally applied by industry, but it usually requires measurable supplemental fuel. Incineration, therefore, is most acceptable where the developed heat can offset other fuel or energy needs. Adsorption, absorption, and condensation techniques - although effective - are limited to exhaust streams with a much narrower range of process characteristics than is incineration.

Process and material changes are the most diverse options available to surface coating industries. Among the available process and material changes are:

- New coating technologies--e.g. water-borne, high-solids, and powder coatings.
- Reduction of air ingestion into the gas stream requiring treatment
- Curing coatings in an inert gas
- More efficient coating application methods

Although these changes offer great promise, almost each one is unique. Consequently the number necessary to meet all product and process requirements is large, and conversion costs are frequently very high. Process and material changes, therefore, can often be implemented only over much longer time periods than those required for installing add-on devices.

Several factors influence the effectiveness, cost and applicability of available control devices or techniques to a given source category. Quite often the characteristics of a particular process or exhaust gas stream dictate the use of certain control techniques. Many control methods are equivalent in reducing pollution but vary in cost. In the latter instances, it is assumed that the operator will select the option that provides the most reduction for the fewest dollars.

Other less obvious factors that are unique to the control of organic emissions influence the selection of a control option. For example, virtually all organics are derived from petroleum, and the increasing cost of crude oil provides considerable economic incentive to both reduce solvent consumption and maximize recovery for use. Other regulatory requirements also can preclude - or dictate - the use of certain options. Insurance and occupational safety requirements that specify maximum allowable organic concentrations for fire prevention and operator safety are examples of such regulatory requirements. Finally, long-term warranties or customer requirements can limit the scope of material or process changes. Section 3 presents a discussion of the control options.

1.4 Economics

Economic aspects of control include not only the investment and annual costs applied to control devices or processes, but also the ability of the affected industries to absorb these costs. Although the affordability question is obviously important, it cannot be addressed in detail because each firm's financial position is unique. It must, however, be addressed by any control official who is considering imposition of a regulation.

Section 4 presents a discussion of the important cost factors along with estimates of the cost to install and operate incineration and carbon adsorption systems. Although generalizations are difficult, the data indicate that, where feasible, carbon adsorption is the most economical approach for low concentrations (about 100 ppm) of organics. For high concentrations (in the range of 25 percent of the low explosive limit), carbon adsorption is preferred if the recovered organics can be reused as solvent; otherwise, incineration with heat recovery is preferred for high concentrations.

Process and material changes are not discussed in Section 4. It is virtually impossible to generalize because of the almost unlimited variety of materials and formulations that are available. For the same reason, costs are estimated in this volume for only the major add-on control options applicable, but not for process or material changes. These options will be discussed in future volumes when considered feasible and reasonable, although in some instances less reasonable examples may be presented to highlight the wide variation in costs that can be incurred. Where possible, the cost effectiveness, that is the cost per unit or organic emission reduction, is presented for each major control option to allow comparison between options and industries.

1.5 Test Methodology

Material balance, the most desirable means of quantifying emissions of volatile organics, is often not practical because of the complexity of reactions, combustion processes, or the dispersed nature of some operations. Where quantification is necessary, a source test will be required. To date, EPA has not adopted a general method for quantification of "total nonmethane hydrocarbons." However, methods have been drafted (and in one case formally proposed) for measurement of gasoline vapor losses from marketing operations. The latter techniques are not usually applicable to the surface coating industry, particularly to baking and curing processes.

In-stack samplers for total nonmethane hydrocarbons are not presently available; therefore, extractive sampling is required. Various techniques are available - all of which rely upon absolute cleanliness of equipment and a minimal elapsed time between sampling and analysis.

Analysis is normally possible when a single compound or very limited number of similar organics are emitted and the gas stream properties are not severe, e.g., gasoline transfer operations. Unfortunately, these favorable conditions occur infrequently. Where known materials are being emitted, gas chromatography appears to be the most useful technique. Where the materials in the gas stream are unknown, techniques which combust the nonmethane hydrocarbons and quantify the resultant carbon dioxide appear accurate. Severe gas conditions (high temperature, for example) greatly increase the difficulty of both sampling and analysis.

Although no test method is universally applicable, testing is usually possible using one or more of the techniques described in Section 5.

1.6 Pollutant Definition and Expression of Emission Limits -- In establishing standards which apply to sources for which specific compliance test methods have not been established, consideration should be given to expressing limitations in absolute terms rather than in terms of a reference method. In this manner, the intent and effect of the standard is clearly established without requiring detailed knowledge of the characteristics of a specific analytical technique as applied to a specific test stream.

When a limitation is expressed in absolute terms, compliance determinations may be made with the most practical technique suitable to the specific case. For screening purposes, a simple tool such as an explosimeter may be satisfactory even though its accuracy may not be more than a factor of two. At the other extreme, gas chromatography combined with mass spectrography could be used where emissions are close to legal limits. In most applications, methods employing FID detectors, or total carbon analysis methods would be used for compliance measurements. In any case, the absolute accuracy of the test technique as applied to the specific source would need to be considered in determining compliance.

As described under "Test Methodology" there are many exhaust streams where it is impractical to apply methods to quantify mass of volatile organic compounds. Therefore, consideration should be given to measuring emissions and expressing standards in terms of carbon (i.e., "xx pounds per hour measured and expressed as carbon"), rather than in terms of true mass. For certain source categories, a more representative molecular weight other than that of carbon could be assigned. For example, limitations on petroleum emissions could be expressed as propane, i.e., "measured as carbon, expressed as C_3H_8." It should be noted that expression of emission limitations in terms of carbon simply broadens the range of potential compliance techniques; it does not necessitate the use of total carbon analysis methods. In fact, applicability and accuracy of the more commonly used measurement techniques involving FID or IR detectors are not in any way diminished by the expression of emission limitations in terms of total carbon. For any stream where an FID analyzer is acceptable, results may, by mathematical manipulation, be "measured and expressed as carbon." The results so expressed are, however, not necessarily an expression of the true volatile organic mass such as would be determined by material balance calculations. An approach based on the use of flame ionization detectors is presented in "Regulation 3," as amended October 2, 1974, Bay Area Air Pollution Control District. A general total carbon analysis method as used by the Los Angeles County APCD is described in "Total Combustion Analysis: A Test Method for Measuring Organic Carbon Dioxide in a Solvent Effluent Control Program," Albert E. Salo, William L. Oaks, and Robert D. MacPhee. Air Pollution Control District, County of Los Angeles August 1974, and "Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors," Albert E. Salo, Samuel Witz, and Robert D. MacPhee, presented at 68th Annual APCD Convention, Boston, Mass., Paper 75-33.2.

In establishing volatile organic regulations, the definitions must state clearly which compounds, if any, are to be exempt. For example, if the purpose is to prevent the emission of oxidant precursors, it would be necessary to identify and delete from consideration carbon monoxide, methane and other carbon compounds that do not contribute to photochemical smog.

In addition, consideration has to be given to the sample collection procedure. The normal procedure is to withdraw a sample, filter any residual particulate and cool, dehumidify or otherwise treat the sample such that it is compatible with the FID, IR, explosimeter, etc. In the most uncomplicated situation, the sample might be withdrawn at ambient temperature and pressure and passed through a filter prior to analysis in an explosimeter. Where the gases are hot and contain organic gases and vapor and some particulate, the sampling procedure is necessarily more complex. A suggested approach for such an operator would be to filter at an elevated temperature, probably 200 to 250°F but not greater than the source temperature, if this is necessary to protect the analytical instrument. If this means cooling the sample, as from an oven operating at 500°F, some condensation of high boiling organics may occur at 250°F but this cannot be avoided. Organics which pass through the filter would then be measured by a suitable analytical technique and considered a volatile organic for enforcement purposes. Thus a regulation should specify whether filterable organic material is to be removed before analysis of organics and should delineate temperature limitations applicable to such filters.

2.0 BACKGROUND INFORMATION

2.1 Oxidants and Volatile Organics

Oxidants are seldom emitted directly into the atmosphere but result primarily from a series of chemical reactions between organic compounds and nitrogen oxides in the presence of sunlight. The factors that determine the concentration of oxidants formed in the atmosphere include the amounts and kinds of organic compounds initially present and the rate at which additional organics are emitted. The very complex chemical reactions involved have been the subject of continuing scientific investigation during the past twenty years, including studies in the atmosphere, laboratory (smog chamber) studies, and computer simulations of the oxidant forming process.

It has been shown in smog chambers that when exposed to a given amount of radiant energy, organic compounds do not form oxidants at the same rate. Given long periods of exposure to radiant energy and sufficient quantities of nitrogen oxides, however, almost all organic compounds will form oxidants. Highly reactive compounds can result in high oxidant levels within a few hours. Less-reactive compounds require longer periods of irradiation to form oxidants. Investigators theorize that these materials may be carried great distances by an air mass before reacting. Thus, they may increase oxidant concentrations at a later time, far downwind of the source.

2.2 Stationary Sources of Volatile Organics

2.2.1 Nationwide Emission Estimates -- No truly comprehensive inventory of organic emissions is available today, although a number of estimates have been made. The most recent estimates made by EPA are given in Table 2.1. These data are obtained from the data file maintained by the National Air Data Branch of the Office of Air Quality Planning and Standards.

The methodology employed to obtain these emission estimates involves the use of air pollutant emission factors applied to nationwide published data on industrial production, fuel consumption, motor vehicle use, and other activity level indicators for particular source types. When appropriate, estimates of average pollutant control efficiency for particular processes are included to calculate controlled emissions.

It is noted from Table 2-1 that the emissions from organic solvent usage comprise a substantial portion of the national total organic emissions.

In Table 2.2 some of the major sources of organic emissions in the United States are listed.

2.2.2 Major Northeastern Sources -- One of the first tasks in this study was development of a reasonably comprehensive list of the major stationary sources in the Northeast where photochemical oxidants are a major concern.

Useful hydrocarbon emissions data had been developed in Region I by the GCA Corporation Technology Division for the Metropolitan Boston Air Quality Control Region (AQCR) and the Rhode Island - Southeastern Massachusetts AQCR. Using this and files from the States of Massachusetts and Connecticut, Table 2-3, a comprehensive list of large (over 100 tons per year) sources was developed.

Table 2.1 NATIONWIDE EMISSION ESTIMATES OF VOLATILE ORGANIC COMPOUNDS - 1975 (PRELIMINARY)

Source Category	Emissions, 10^6 tons/yr	
Transporation		11.7
Highway	10.0	
Non-Highway	1.7	
Stationary Fuel Combustion		1.4
Electric Utilities	0.1	
Other	1.3	
Industrial Processes		
Chemicals	1.6	
Petroleum Refining	0.9	
Metals	0.2	
Other	0.8	
Miscellaneous		13.4
Organic solvents	8.3	
Oil and Gas Production and marketing	4.2	
Solid Waste	0.9	
Open Buring		1.0
Forest Wildfires	0.6	
Forest Managed Burning	0.2	
Agricultural Buring	0.1	
Coal Refuse Burning	0.1	
Total		31.0

TABLE 2-2. TYPICAL SOURCES OF VOLATILE ORGANICS WITHIN INDUSTRIAL CATEGORIES

Fuel combustion, burning and solid waste incineration

- Boilers (coal, oil and gas)
- Wood combustion
- Stationary engines
- Agricultural burning
- Solid waste incineration
  - (municipal, industrial, and domestic)
- Coal refuse
- Orchard heaters

Petroleum refining, distribution, and marketing

- Miscellaneous point sources - refineries
- Vacuum distillation
- Process gas combustion
- Crude, gasoline, distillate, naphtha, etc.
  - Transfer losses
  - Working losses
  - Breathing losses
  - Refueling losses

Chemical manufacturing

- Ammonia
- Carbon black
- Charcoal
- Paint, varnish, and printing ink
- Pharmaceuticals
- Synthetic resins, fibers and plastics
- Ethyl benzene
- Ethyl oxide
- Acrylonitrile
- Formaldehyde
- Ethylene dichloride
- Phthalic anhydride
- Maleic anhydride
- Ethylene
- Propylene
- Butadiene
- Ethane, butane, propane
- Benzene, toluene, xylene

Evaporation of organic solvents

- Degreasing
- Drycleaning
- Graphic arts
- Metal coating
  - Auto assembly
  - Can manufacturing
  - Coil coating
  - Appliances
  - Machinery
  - Commercial products
  - Furniture
  - Pesticide Manufacture and use
  - Vegetable oil manufacturing
- Textile coating and finishing
  - Dyeing
  - Scouring
  - Rubberizing
  - Carpet manufacturing
- Paper and film coating
  - Coated papers
  - Water proofing
  - Pressure sensitive tapes
  - Magnetic tape
- Wood finishing
  - Furniture
  - Plywood and panel coating
- Tire manufacturing

Other industrial sources

- Wood processes
  - Kraft pulping
  - Plywood
- Metallurgical processes
  - Cast iron foundries
  - By-product coke
- Beer and whiskey production
- Mineral processes
  - Asphalt
  - Fiberglas
  - Mineral wool
- Food processing
- Direct firing of meats
- Deep fat frying

Additional information supplied by Regions II, III and V was generally in the form of "source-categories-considered-to-be-significant" with little specific data on emission rates.

Table 2-3 summarizes the information obtained from EPA's Regional Offices. Again, although the data are not necessarily comprehensive nor all inclusive, the recent emission inventories tend to confirm that these sources emit large amounts of volatile organics. The listing in Tables 2-3 is not in order of amount of emissions or priority.

Table 2-3 MAJOR INDUSTRIAL ORGANIC EMISSION SOURCE CATEGORIES IN THE NORTHEASTERN U.S.

Paper coating
Fabric coating and finishing
Automotive assembly
Shipbuilding and repair
Degreasing
Drycleaning
Graphic Arts Application
Tire manufacturing
Can manufacturing
Coil coating
Petroleum refining
Magnetic tape coating
Steel production
Various synthetic organics production
  (plastics, rubbers, resins, etc.)
Pharmaceutical production

2.3 References for Chapter 2

1. Impact of New Source Performance Standards on 1985 National Emissions from Stationary Sources. Vol. 1, The Research Corporation of New England (TRC). Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C. under Contract No. 68-02-1382, October 1975.

2. Source Assessment: Prioritization of Air Pollution from Industrial Surface Coating Operations. Monsanto Research Corporation, Dayton, Ohio. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C. under Contract No. 68-02-1320 (Task 14). Publication No. 650/2-75-109-a. February 1975.

3. CONTROL TECHNOLOGY

3.1 INTRODUCTION

Volatile organic emissions can be reduced by add-on control devices and by process and material changes. This section reviews the most commonly used methods; important technical aspects of each method are discussed and problems and limitations considered.

3.2 ADD-ON EQUIPMENT

3.2.1 Carbon Adsorption

3.2.1.1 Introduction -- Carbon adsorption uses a physical phenomenon to separate organic vapors from a gas stream and to concentrate these vapors to a more manageable form. The theory of carbon adsorption is discussed, variables affecting carbon adsorption explored, and design and operation discussed along with problem areas.

Carbon adsorption is applicable to most organic-emitting industries studied (with a few solvents excepted) but the costs and difficulties will vary with the specific industry.[1] A more complete discussion of applicability in specific industries is given in additional volumes.

The term "sorption" applies to two types of phenomena: (1) where vapor molecules are concentrated by adsorption on the surface, and (2) where vapors are concentrated by absorption of the vapor molecules into the mass of the sorbent. Adsorption is accomplished using four different types of materials: (1) chemically reactive adsorbents (2) polar adsorbents (3) molecular sieves, and (4) nonpolar adsorbents.

When adsorption is accompanied by chemical reaction, the process is termed "chemisorption," an exothermic process where molecules can only be one layer thick. It has been used for odorous sulfur compounds and some olefins but has little application at this time for organic solvent control.

When adsorption is not accompanied by chemical reaction, the process is termed physical adsorption. In general, polar adsorbents adsorb polar molecules (e.g., water) preferentially, while nonpolar adsorbents adsorb nonpolar molecules (e.g., hydrocarbon) preferentially. Physical adsorption is less selective than chemisorption, the process is reversible and vapor molecules can be adsorbed in more than one layer on the surface. The force of adsorption is the Van der Waals force. Molecules of any solid are attracted to each other and the surface molecules of the adsorption medium are subject to unbalanced forces that cause vapor or liquid molecules to be attracted to the surface. These forces can be induced in such a way that more than one layer of molecules can be adsorbed. It must be noted that in practice, adsorption takes place through a combination of molecular attraction (Van der Waals forces) and capillary condensation of the vapors being adsorbed in the pores provided by the extended surface of the adsorbent. Although activated carbon does not enter into chemical reaction with the adsorbed vapors, it does catalyze hydrolysis and degradation reactions of certain organic solvents, such as ketones.

Activated carbon is the only physical adsorbent presently in widespread use for organic vapor collection. It is a nonpolar adsorbent although it has some adsorptivity for water.

3.2.1.2 Theory of Carbon Adsorption

Activated carbon -- Activated carbon can be produced from a variety of carbonaceous materials, its characteristics depend on the raw material and the activation process. Carbon is activated by oxidation of portions of the carbon with steam or chemicals. The end-product of activation is a material with a fine, partially interconnected pore structure that has a very large surface area.

Primary variables -- The surface area of the activated carbon is the primary variable. The larger the available area, the larger the adsorption capacity of the carbon, other things being equal. A typical activated carbon may have a surface area of 1100 square meters per gram.

The capacity of carbon is often represented by "adsorption isotherms" such as Figure 3-1 showing the effect of increasing molecular weight of organics on carbon capacity. The isotherms level out as the micropores are filled. For pollution control situations, the range of interest is below a partial pressure of 10 mm of Hg. The effect of temperature on adsorption is shown by Figure 3-2.

The Polanyi equation can be used for predicting the effect of inlet pollutant concentration on adsorption capacity in the low concentration range. It can be expressed as follows:

$$\text{Adsorptive Capacity in } \frac{\text{g solvent}}{\text{g carbon}} \propto \frac{V_m}{T \log (C_o/C_i)}$$

Where V_m = liquid molar volume of pollutant at normal boiling point

T = absolute temperature

C_o = concentration of saturated vapor

C_i = initial pollutant vapor concentration into adsorber

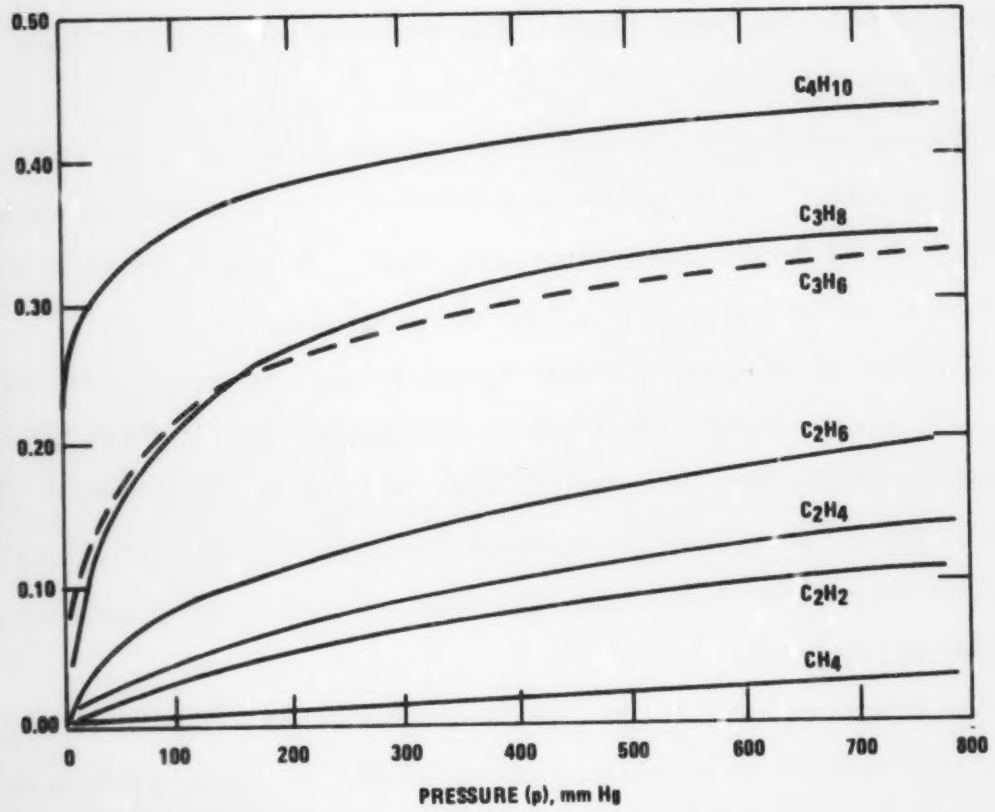

Figure 3-1. Adsorption isotherms of hydrocarbon vapors (amount adsorbed, ω, at pressure, p, on type Columbia L carbon at 100°F, liquid volume of ω at boiling temperature).[1]

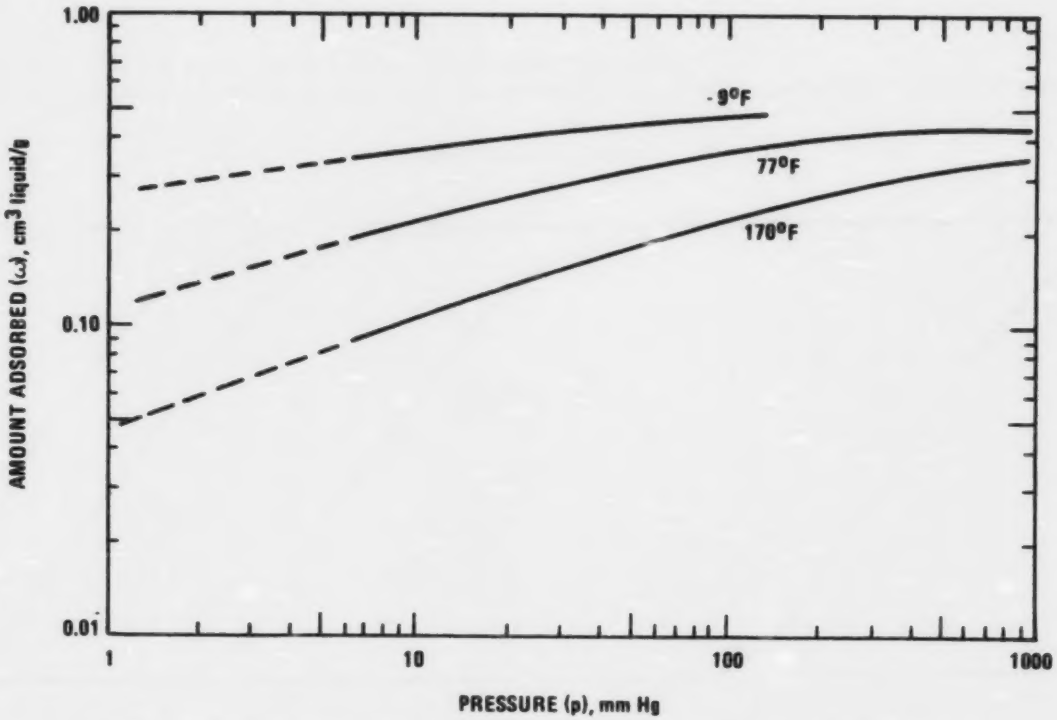

Figure 3-2. Adsorption isotherms of butane at three temperatures on Pittsburgh BPL type carbon (amount, ω, adsorbed at pressure, p).[1]

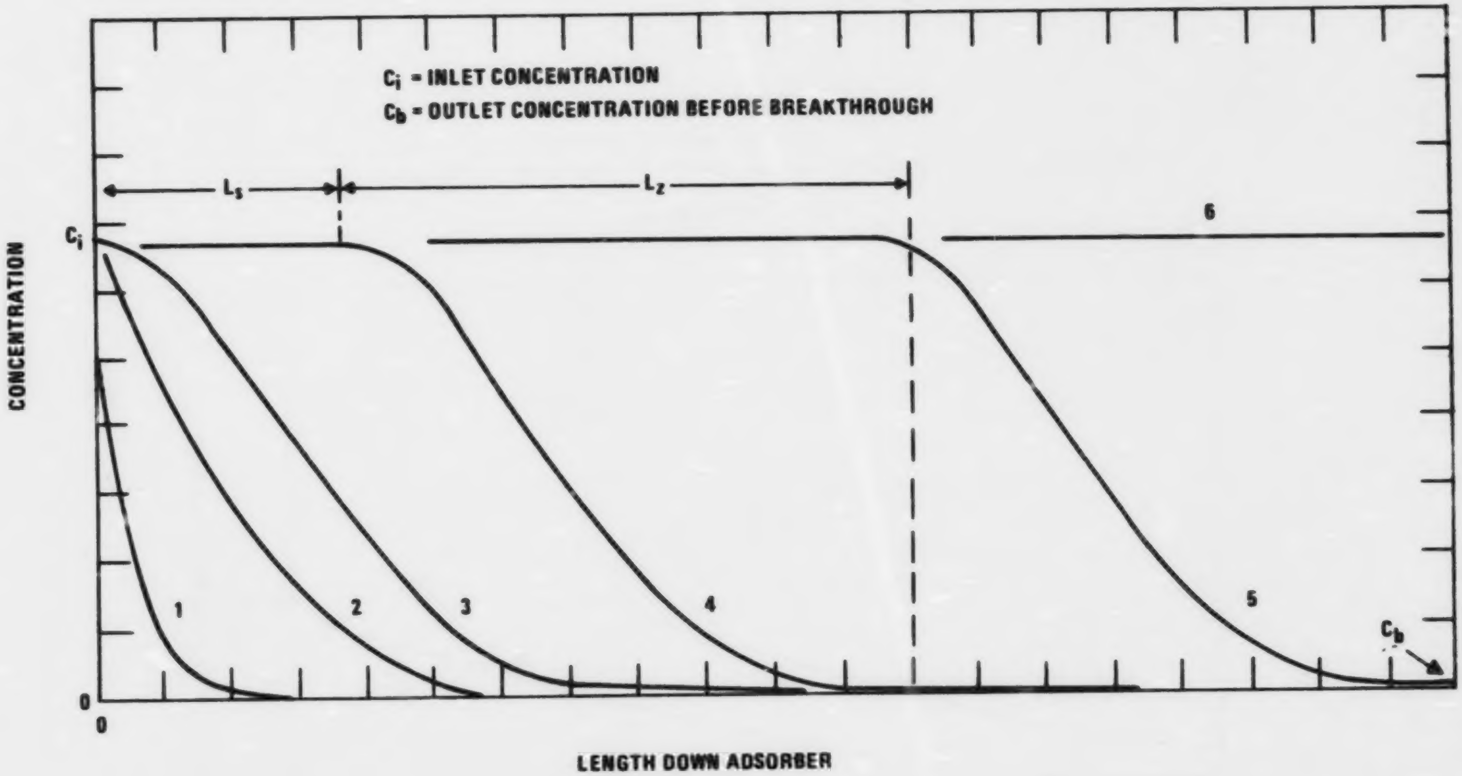

Figure 3-3. Movement of vapor concentration distribution curve in carbon bed with increased adsorption time. For curve 4, L_s is the saturated zone and L_z is the adsorption zone.[1]

This equation shows that low temperature, high V_m, and high concentrations of the organic being adsorbed all tend to increase capacity.

Dynamic adsorption -- For a fixed-bed carbon adsorber, the concentration profile in the bed changes with time as the capacity of the bed is approached. Figure 3-3 shows an example of organic vapor concentration profiles for five different elasped times after regeneration of the carbon. Curve number 4 represents the "breakthrough" time, i.e., the time when organic vapor concentration at the outlet of the adsorber reaches a defined level (usually 1 percent of the inlet concentration). In Figure 3-4, the exit concentration versus time is shown for a specific case. The breakthrough time is 600 minutes and corresponds to Curve 4 of Figure 3-3. A time of 1000 minutes corresponds to Curve 5 of Figure 3-3. The bed should be regenerated at 600 minutes although full utilization of the bed is not realized until 1000 minutes. The length of the bed where active adsorption occurs is called the adsorption zone. Length of this zone is usually about 2 inches.

For exhaust streams containing multiple solvents, vapors of higher V_m will displace vapors of lower V_m. If the vapors have very different V_m, adsorption will be as if each solvent was adsorbed independently in a bed as shown in Figure 3-5. If the vapors are close in V_m there will be co-adsorption as shown in Figure 3-6. In either case, the compound with the lowest V_m will exit the adsorber bed first. Bed depth for multiple solvents can be estimated from summation of the bed depths necessary to adsorb each of the vapors if those vapors were alone in the gas stream. All of the adsorption zones must be considered in the calculation of necessary bed depth.

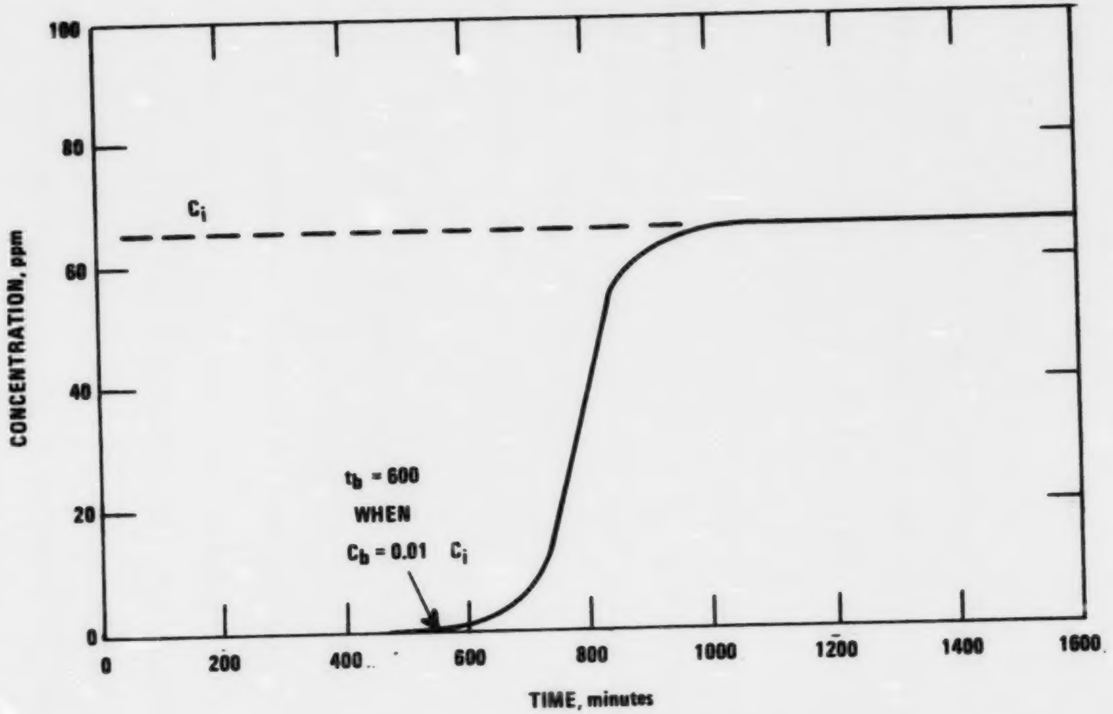

Figure 3-4. Effluent concentration curve of butane vapor from activated carbon bed as function of time.[1]

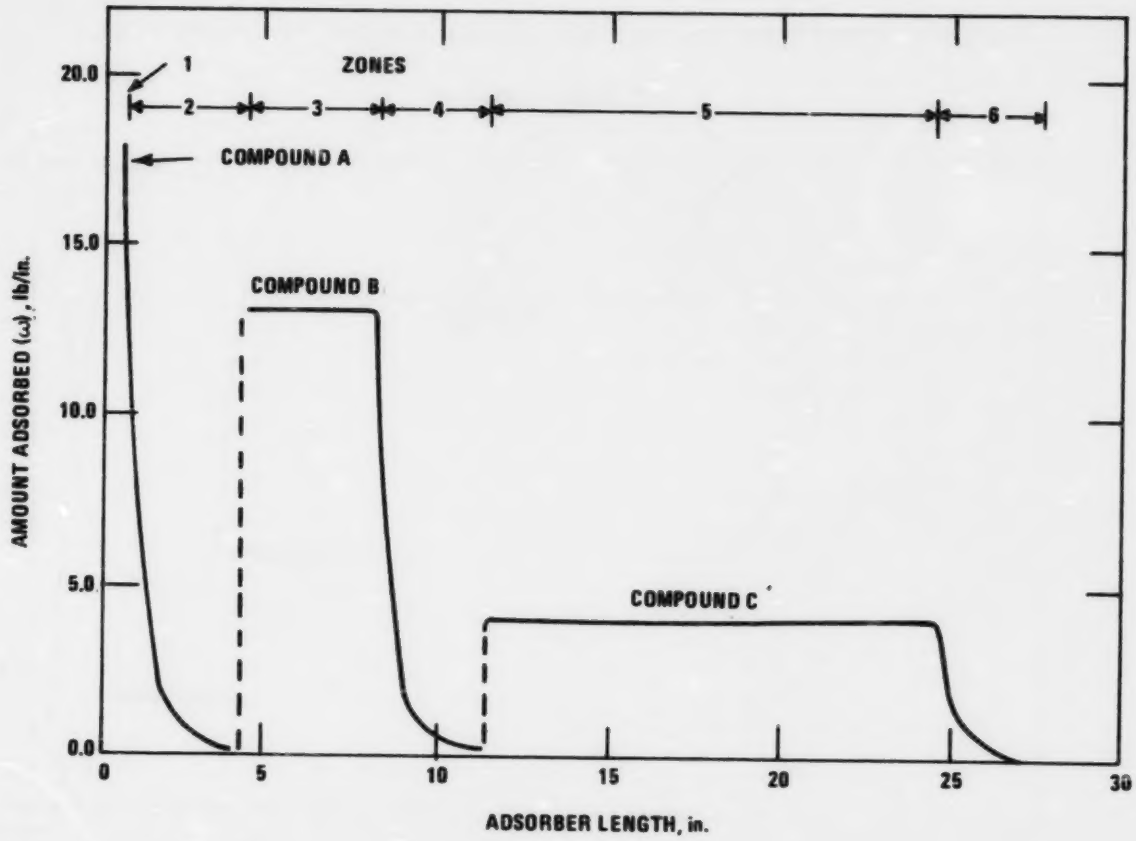

Figure 3-5. Adsorbed vapor profile in activated carbon bed after steady state is established but with no coadsorption. The odd numbered zones are saturated with the respective solvents, and the even numbered zones are the adsorption zones.[1]

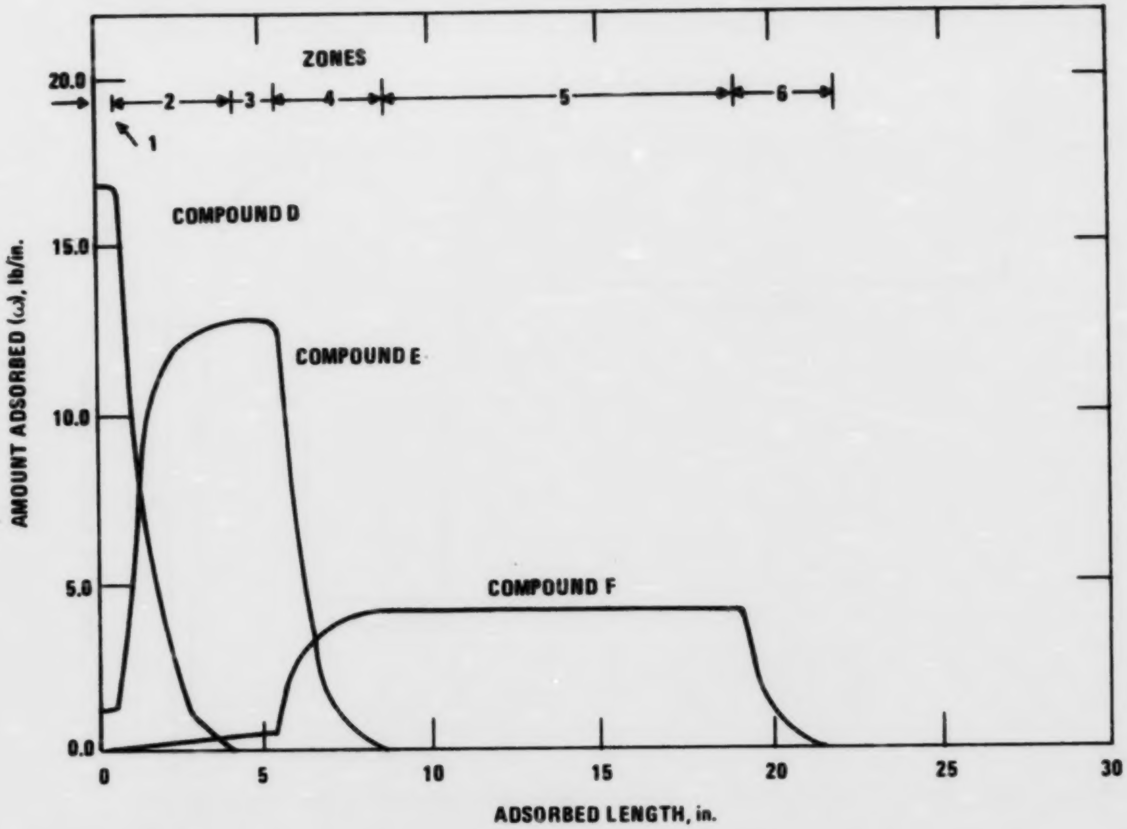

Figure 3-6. Adsorbed vapor profile in activated carbon bed after steady state is established with coadsorption.[1]

3.2.1.3 Regeneration -- For concentrations greater than a few parts per million, carbon must be used many times for economic reasons. To remove adsorbed vapors and reuse the carbon, regeneration is necessary. Regeneration is the removal of adsorbed organics from the carbon and is accomplished by bringing the bed to near equilibrium at a higher temperature. Typical regenerants are steam, hot air, and hot inert gas. The hotter the regenerant and the longer the regeneration, the more adsorbed solvent will be removed (desorbed) from the carbon bed. There is an economic optimum where adequate desorption occurs at reasonable energy cost. The residual solvent in the bed after regeneration is called the "heel" and "working capacity" the difference between full capacity and the heel. Regeneration is typically about 50 percent complete for each cycle under proper (or economic) operation. To optimize the frequence of regeneration, an automatic device that signals breakthrough may be useful if the size of the adsorber warrants.

Steam regeneration -- Steam is the most widely used regenerant. The bed is closed off from pollutant flow, and steam is introduced into the bed. The steam and the pollutant vapors are routed to a condenser after which they can usually be separated by gravity or distillation. Steam regeneration has the advantage of leaving the bed wet. By control of the degree of wetness in the bed, various degrees of gas cooling can be accomplished. In a variation of this scheme, steam and pollutant can be incinerated without condensation.

Noncondensible gas regeneration -- As inlet concentration decreases, the bed capacity is reduced. In order to achieve adequate working capacity for low concentrations, the heel must be minimized with consequent increased steam usage. Figures 3-7 and 3-8 show the effect of vapor concentration on the steam requirement for regeneration. The two compounds (propanone and 4-methyl-2 pentanone) span the range of V_m for which carbon adsorption is applicable. For concentrations less than 700 ppm, air or inert gas should be considered for regeneration, especially if (1) the adsorbed solvent has no value, (2) the material has appreciable miscibility with water, or (3) the solvent does not contain large amounts of halogen-, nitrogen- or sulfur-containing compounds.

If a noncondensible gas is used for regeneration, the organics can be removed by condensation, adsorption, and/or incineration. Condensation of virtually all organics in a stream is possible if the stream is cooled to a low enough temperature. A more practical approach is to condense a portion of the vapor and to recycle the remainder back through the operating bed. A schematic of this system is shown in Figure 3-9.

Secondary adsorption of the vapors in a smaller adsorber offers a possible method of recoving vapors from a dilute source. The primary adsorber is regenerated by heated inert gas, yielding a gas stream in which the vapor concentration is about 40 times as high as in the original stream. After cooling, this stream can then be passed through a secondary adsorber which is regenerated by steam and the organic material recovered. Reference 1 gives further details for this scheme.

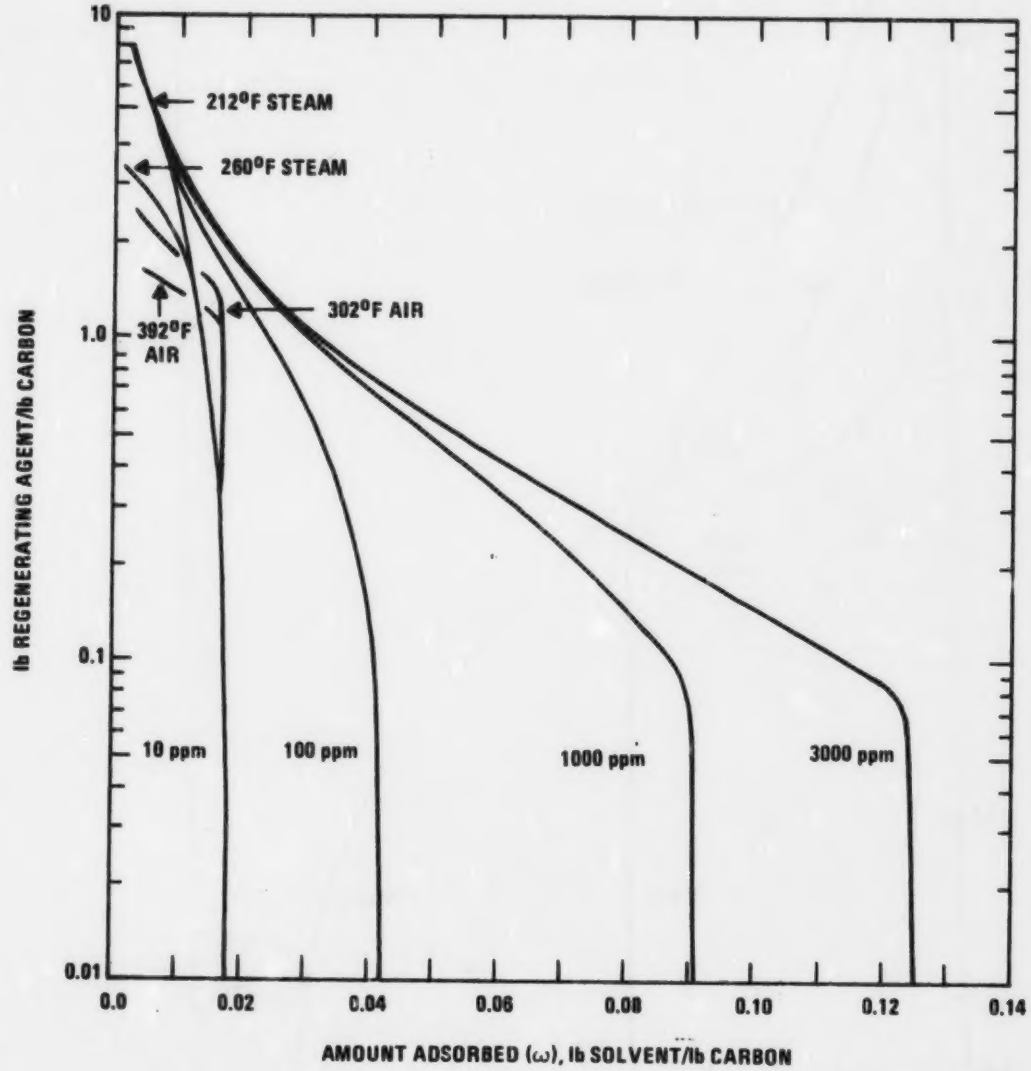

Figure 3-7. Amount of regenerating agent required to regenerate BPL V type carbon equilibrated with propanone at varied concentrations.[1]

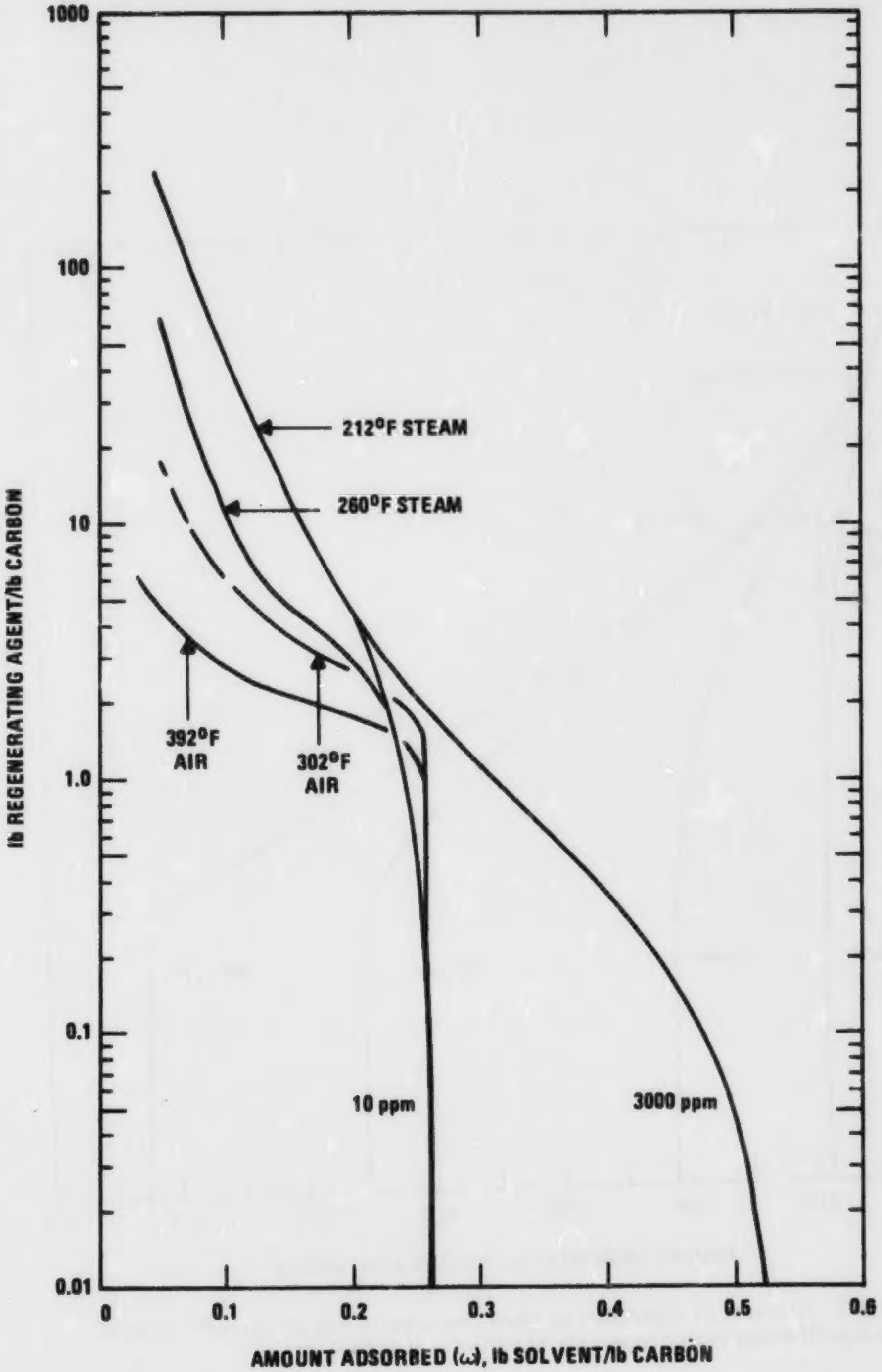

Figure 3-8. Amount of regenerating agent required to regenerate GI type carbon equilibrated with 4-methyl-2-pentanone at 10 and 3000 ppm.[1]

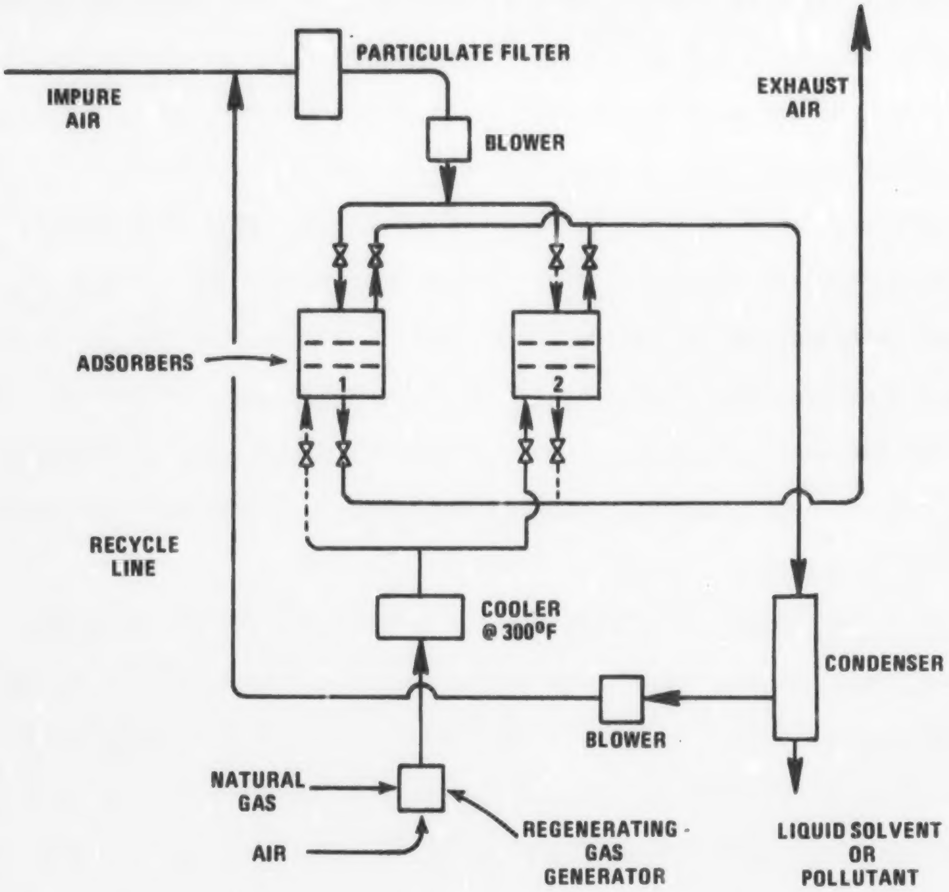
PARTICULATE FILTER
IMPURE AIR
EXHAUST AIR
BLOWER
ADSORBERS
1
2
RECYCLE LINE
COOLER @ 300°F
CONDENSER
BLOWER
NATURAL GAS
AIR
REGENERATING - GAS GENERATOR
LIQUID SOLVENT OR POLLUTANT

Figure 3-9. Air pollution control system utilizing carbon-resorb with gas regeneration, condensation, and recycle of uncondensed vapor.[1]

3.2.1.4 Problem Areas with Carbon Adsorption -- Several problems are encountered in systems controlling the bake ovens which follow most surface coating operations. Thermal breakdown of the solvents and/or resins can generate a range of low V_m compounds that cannot be adequately adsorbed; examples are formaldehyde, methanol, and acetic acid. Polymerization reactions may produce tar-like products that will condense at the operating temperatures of carbon adsorbers and not be desorbed, causing fouling. These complications, if present, do not make carbon adsorption impossible for ovens, but they will necessitate precautions or lower carbon life.

Compounds such as acetone, methyl ethyl Ketone (MEK), and phenol, may cause problems because of high heat of adsorption. With proper design, however, problems can be avoided. The main requirement is the use of a wet bed and a controlled relative humidity in the inlet gases to provide a heat sink for the adsorbed vapors. Dimethyl formamide (DMF) and nitropropanes are a more serious problem; carbon adsorption is probably not applicable where these solvents are used.

Reuse of solvent -- Unless a single solvent is used and breakdown is avoided, reuse of the solvent may not be feasible. Distillation is possible, but the complexity and cost are so variable that it is difficult to generalize. Reuse of mixed recovered solvents is unlikely if the source is a "toll coater" or "jobber" where many solvents are run on the same machine. In general, it has been assumed in this analysis that if the solvent is recovered, it has fuel value only.

Particulates -- Particulate matter, if allowed to enter the carbon bed, can coat the carbon or plug the voids between carbon particles. Adsorbtivity is decreased and pressure drop increases. The net result is that the carbon must be replaced or cleaned more often. Siliconized coatings cause especially difficult problems.

A solution to a particulate problem is precleaning of the gas. Fabric collectors, mist eliminators, or scrubbers may be used. The particulate may be very small in particle size, viscous or tacky and hence difficult to remove. Mist eliminators may be used if the particulate is a liquid. If the condensed vapors harden at the operating temperature of the particulate collector, frequent cleaning may be necessary.

Temperature -- Carbon capacity is greater at lower temperatures. Usually 100°F is considered the maximum entry temperature. Cooling may be accomplished by direct water sprays or by cooling coils. If condensible gases are present, a spray cooler and mist eliminator should be placed ahead of the adsorber if possible.

Humidity -- Although carbon preferentially adsorbs organic materials, water will compete with the organics for adsorption sites. To minimize this, relative humidity must be kept below about 50 percent. A minimum of 20 to 40 percent relative humidity should be maintained, however, especially if ketones are to be adsorbed. If gases are hot and wet, cooling followed by some reheat may be necessary. Water formed by fuel combustion must be considered.

Concentration -- The range of concentrations for which carbon adsorption is applicable is limited. The increased operating cost of low concentrations has been discussed. There is also a potential problem with high concentrations. Adsorption is always an exothermic phenomenon; typically 200 to 300 Btu is generated per lb of solvent adsorbed. If sufficient air is not present to carry this off, the bed can overheat. This can result in poor adsorption and, in extreme cases, bed fires. For concentrations over 25 percent of the lower explosive limit (LEL),* heating of the bed must be considered in calculations. The problem can be minimized by leaving the bed wet with water.

3.1.2.5 Equipment Design and Operation -- Although there are a great variety of possible schemes for carbon adsorption, most applications are similar in design.

The face velocity is defined as the flow rate divided by cross sectional area of the bed. At high face velocities, the pressure drop increases and is the controlling factor in practical cases. Flow velocities for regenerable systems vary from 30 to 110 feet per minute. The sizes of necessary vessels are shown in Table 3-1 assuming a face velocity of 90 feet per minute. Note that for larger beds, design is for horizontal flow. In evaluating the applicability of carbon adsorption to a source, floor or roof space must be considered.

Table 3-1. TYPICAL BED SIZES FOR CYLINDRICAL CARBON ADSORBERS

Flow rate, cfm	Size of bed
1,000	4 ft diameter - vertical vessel
3,000	7 ft diameter - vertical vessel
10,000	12 ft diameter - vertical vessel
30,000	12 ft diameter/28 ft long - horizontal vessel

---

*The lower explosive limit of a sustance is the lowest volume percent concentration of the vapor in air which can be ignited at 70°F and normal atmospheric pressure.

The usual practice is to install at least two adsorbers and operate so that one is adsorbing while the other is regenerating. The largest vessel that can be factory assembled handles about 30,000 cfm. Thus for larger sources the designer has to choose between multiple packaged units and field assembled adsorbers. The materials of construction depend on the source to be controlled. If carbon dioxide is present, carbonic acid may be formed. If halogenated compounds are formed, halogen acids may form. Formaldehydes can yield formic acid. Often a stainless or high nickel steel is required.

Bed depths vary with the organic vapor type, with the concentration of organic vapors and with the desired time between regenerations. The lower the V_m, the lower the capacity of the carbon. Higher concentrations increase the capacity of the carbon, but also increase the amount of organic vapor to be adsorbed per unit volume of gas. The net effect is that at higher concentrations, the bed must be deeper for a given vapor, face velocity, and time between regeneration. Bed depths typically range from 1-1/2 to 3 feet but can be less at low concentrations. Cycle times for regenerable systems usually run about 2 hours. Higher flow rates cause the adsorption zone to be longer. For the bed depth range of interest for regenerable systems, this length of 2 to 4 inches will not be significant in comparison with total bed depth.

For a system in which there are no compounds with V_m greater than 190 cm^3/mol, and no polymer formers, or excessive particulates reaching the carbon, a carbon life of 5 to 10 years can be expected.

3.1.2.6 Control Efficiency -- Where carbon adsorption is applicable, 90 percent removal in the carbon adsorber is commonly attainable.

3.1.2.7 Adverse Environmental Effects of Carbon Adsorption -- If the organic solvents to be recovered are miscible with water, a potential water pollution problem exists. Ways to avoid this are to treat the water or to incinerate the desorbed vapor, together with the steam or air purge.

If incineration is used with solvents containing halogens, sulfur, or nitrogen compounds, acid gases, SO_x and NO_x will result.

3.1.2.8 Effect of Technical Assumptions on Cost Models -- The major technical assumption made for carbon adsorbers in the calculations in Section 4.2.3.2 was the assumption that the organic vapor was 50 percent benzene and 50 percent hexane by volume. The important parameters for these solvents are given in Table 3-2.

Table 3-2. PROPERTIES OF HEXANE AND BENZENE

Solvent	Molar volume (V_m), cm^3/mol	Lower explosive limit, ppm
Hexane	140	12,000
Benzene	95	14,000

These compounds are in the middle of the applicable range for carbon adsorption and are also among the most widely used organic compounds. If the solvents used have a higher V_m, capacity of the bed is increased, with subsequent increased difficulty of regeneration. If solvents used have a lower V_m, capacity is less and regeneration easier. Within the applicable range of V_m for carbon adsorption, costs would not vary greatly from the assumptions given.

The assumption of a hexane/benzene solvent involves some secondary assumptions. Steam can be used for regeneration, at a fairly low steam to solvent ratio. The particular solvents can be separated easily and cheaply from the condensed steam by decantation. Thus, effluent water contains no measurable organics. If the solvent contains water soluble components additional equipment and operations will be required, such as: (1) distillation equipment plus water treatment; or (2) incineration of the desorbed vapor/steam mixture; or (3) hot air regeneration followed by incineration. These options can increase costs markedly. Because solvent formulations are extremely varied, there is insufficient information upon which to base reliable estimates of the increased costs under these conditions.

Prior to the adoption of Rule 66 solvents with adsorption properties similiar to hexane and benzene were quite common. However, reformulation led to the widespread introduction of oxygenated components (alcohols, ketones, esters, and ethers) into most solvent mixtures. Most of these compounds have significant solubility in water. Therefore, a solvent mixture similiar to benzene/hexane is probably the exception rather than the rule.

The cost assumptions do not include any particulate removal equipment. If particulates are present in amounts sufficient to require removal, the system cost will be increased significantly.

The cost of steam for desorption is based on compounds which desorb readily. If compounds which are difficult to desorbe are encountered, steam costs will be increased.

3.2.2 Incineration

3.2.2.1 Introduction -- Incineration destroys organic emissions by oxidizing them to carbon dioxide and water vapor. Incineration is the most universally applicable control method for organics; given the proper conditions, any organic compound will oxidize. Oxidation proceeds more rapidly at higher temperatures and higher organic pollutant content. Incinerators (also called afterburners) have been used for many years on a variety of sources ranging in size from less than 1000 scfm to greater than 40,000 scfm.

Use of Existing Process Heaters for Incineration -- The use of existing boilers and process heaters for destruction of organic emissions provides for the possibility of pollution control at small capital cost and little or no fuel cost. The option is, however, severely limited in its application. Some of the requirements are:

1. The heater must be operated whenver the pollution source is operated; will be uncontrolled during process heater down time.
2. The fuel rate to the burner cannot be allowed to fall below that required for effective combustion. On-off burner controls are not acceptable.
3. Temperature and residence time in the heater firebox must be sufficient.
4. For proper control, the volume of polluted exhaust gas must be much smaller than the burner air requirement and be located close to the process heater. For most plants doing surface

coating, especially if surface coating is their main business, the combustion air requirement is smaller than the coater-related exhaust. In many diversified plants, the coating operation may be distant from heaters and boilers.

5. Constituents of the coating-related exhaust must not damage the internals of the process heater

Few boilers or heaters meet these conditions.

Use of add-on incinerators -- In noncatalytic incinerators (sometimes called thermal or direct flame incinerators), a portion of the polluted gas may be passed through the burner(s) in which auxiliary fuel is fired. Gases exiting the burner(s) in excess of 2000°F are blended with the bypassed gases and held at temperature until reaction is complete. The equilibrium temperature of mixed gases is critical to effective combustion of organic pollutants. A diagram of a typical arrangement is shown in Figure 3-10.

The coupled effect of temperature and residence time is shown in Figure 3-11. Hydrocarbons will first oxidize to water, carbon monoxide and possibly carbon and partially oxidized organics. Complete oxidation converters CO and residuals to carbon dioxide and water. Figure 3-12 shows the effect of temperature on organic vapor oxidation and carbon monoxide oxidation.

A temperature of 1100 to 1250°F at a residence time of 0.3 to 0.5 second[2] is sufficient to achieve 90 percent oxidation of most organic vapors, but about 1400 to 1500°F may be necessary to oxidize methane, cellosolve, and substituted aromatics such as toluene and xylene.[2]

Design -- Incineration fuel requirements are determined by the concentration of the pollutants, the waste stream temperature and oxygen

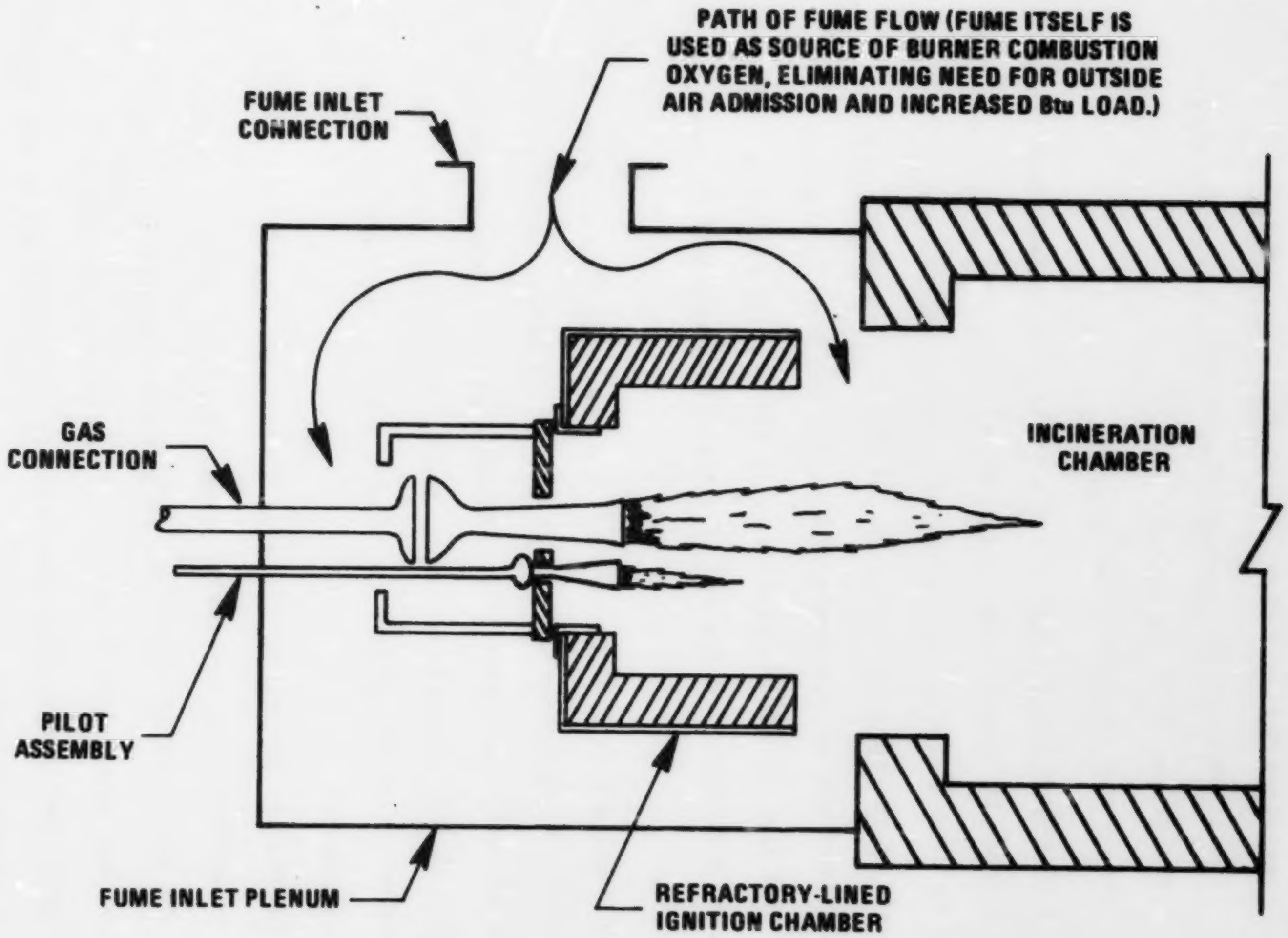
PATH OF FUME FLOW (FUME ITSELF IS USED AS SOURCE OF BURNER COMBUSTION OXYGEN, ELIMINATING NEED FOR OUTSIDE AIR ADMISSION AND INCREASED Btu LOAD.)
FUME INLET CONNECTION
GAS CONNECTION
INCINERATION CHAMBER
PILOT ASSEMBLY
FUME INLET PLENUM
REFRACTORY-LINED IGNITION CHAMBER

Figure 3-10. Typical burner and chamber arrangement used in direct-flame incinerator.

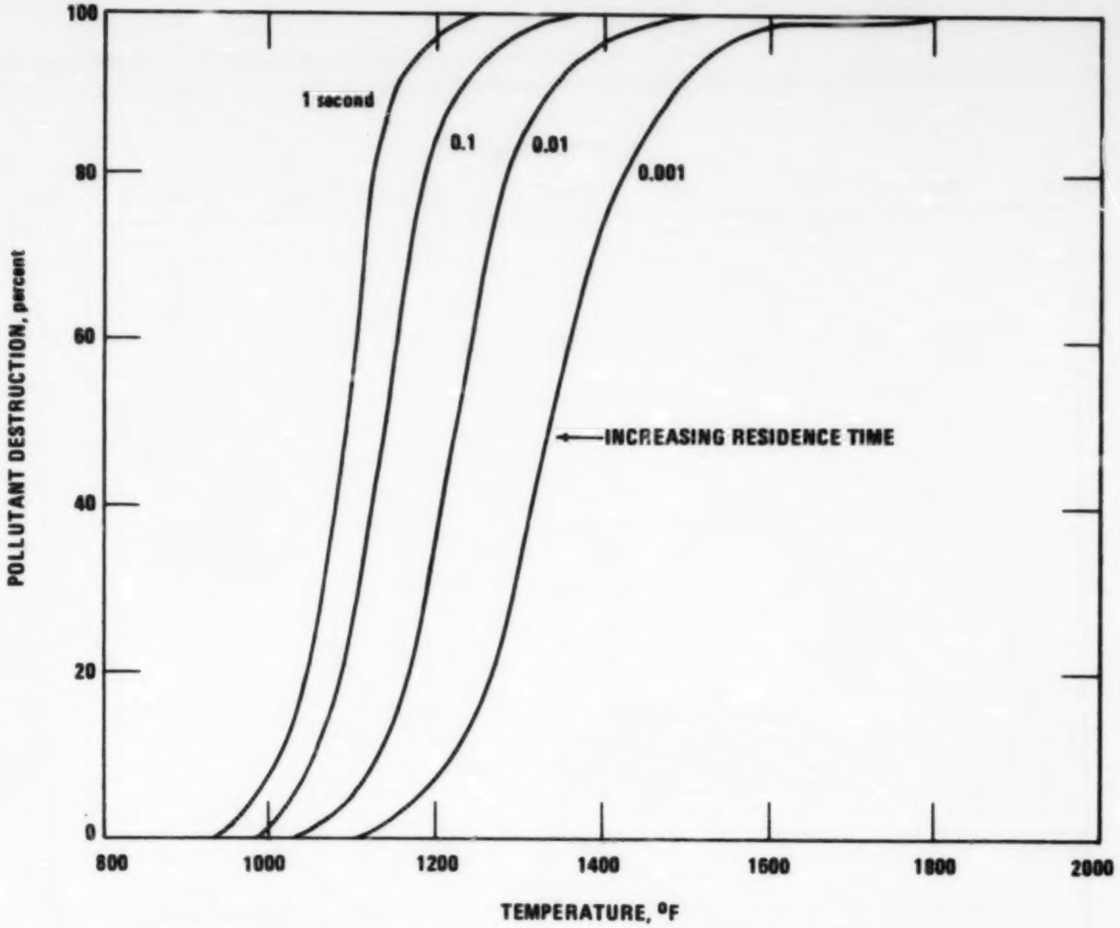

Figure 3-11. Coupled effects of temperature and time on rate of pollutant oxidation.[1]

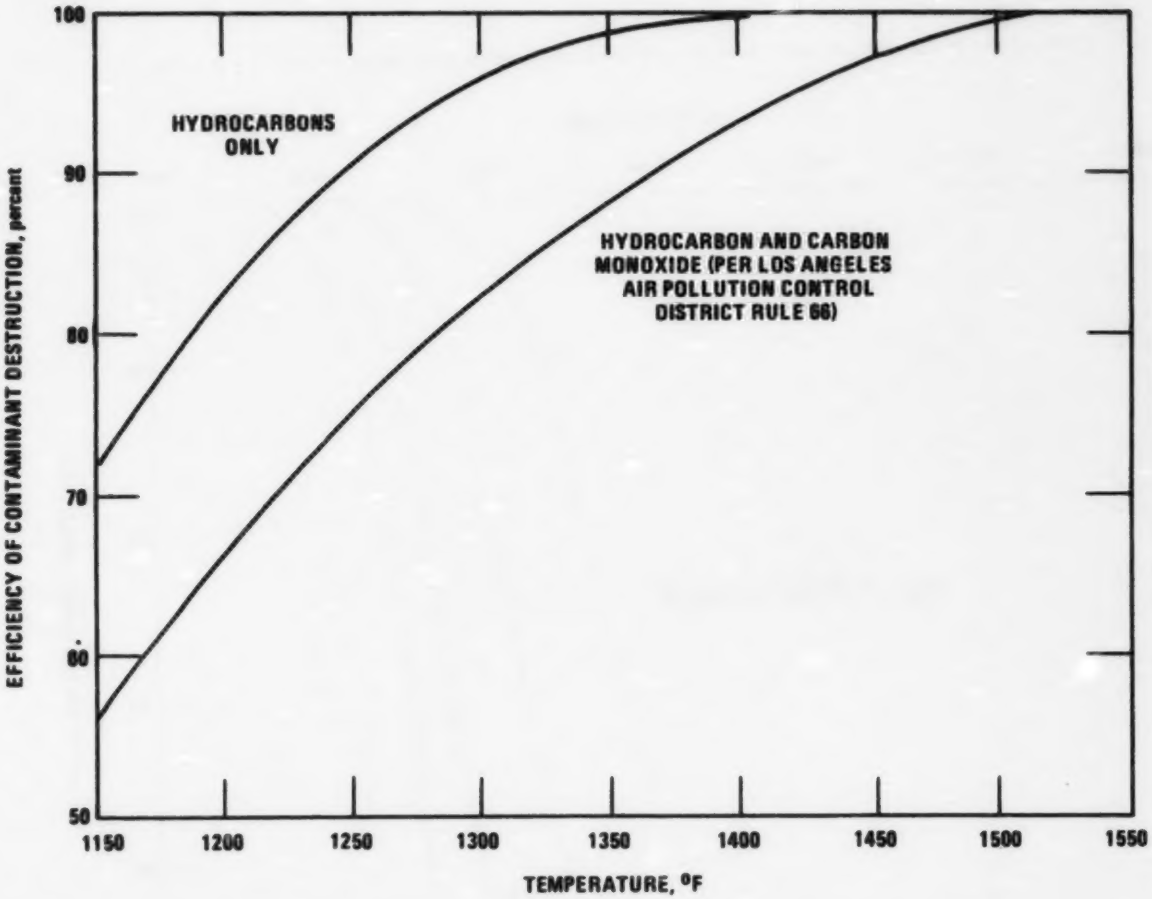

Figure 3-12. Typical effect of operating temperature on effectiveness of thermal afterburner for destruction of hydrocarbons and carbon monoxide.[1]

level, and the incineration temperature required. For most organic solvents, the heat of combustion is about 0.5 Btu/scf for each percent of the LEL. This is enough to raise the waste stream temperature about 27.5°F for each percent of the LEL (at 100 percent combustion). Thus, at 25 percent of the LEL, the temperature rise will be 620°F for 90 percent conversion.

Fuel -- Natural gas, LPG and distillate and residual oil are used to fuel incinerators. The use of natural gas or LPG results in lower maintenance costs; at present, natural gas also is the least expensive fuel. However, the dwindling natural gas supplies make it almost a necessity to provide newly installed incinerators with oil-burning capabilities.

In most cases where natural gas or LPG is not available, incinerators are fixed with distillate fuel oil; residual oil is seldom employed. Oil flames are more luminous and longer than gas flames, thus require longer fireboxes. Almost all fuel oils, even distillate, contain measurable sulfur compounds. Residual oils generally have greater sulfur and particulate contents and many have appreciable nitrogen fractions. Sulfur oxides, particulates and NO_x in combustion products from fuel oil increase pollution emissions and cause corrosion and soot accumulation or incinerator work and heat transfer surfaces.

Heat recovery -- Heat recovery offers a way to reduce the energy consumption of incinerators. The simplest method is to use the hot cleaned gases exiting the incinerator to preheat the cooler incoming gases. Design is usually for 35 to 90 percent heat recovery efficiency.

The maximum usable efficiency is determined by the concentration of the organics in the gases, the temperature of the inlet gases, and the maximum temperature that the incinerator and heat exchangers can withstand.

In a noncatalytic system with a primary heat exchanger, the preheat temperature should not exceed 680°F, a 25 percent LEL, in order to limit incinerator exit temperatures to about 1450°F for the protection of the heat exchanger. The auxiliary fuel would heat the stream about 150°F and oxidation of the solvent would heat it about 620°F for an exit temperature of 680 + 150 + 620 = 1450°F. At 12 percent LEL the preheat temperature should not exceed 930°F. Most burners have not been designed to tolerate temperatures above 1100°F.

There are several types of heat recovery equipment using different materials at various costs. The most common is the tube and shell heat exchanger. The higher temperature exhaust passes over tubes, which have lower temperature gas or liquid flowing through the tubes; thus increasing the temperature of that gas or liquid. Another method uses a rotating ceramic or metal wheel whose axis is along the wall between two tunnels. Hot exhaust flows through one tunnel and heats half of the wheel. Lower temperature air flows through the other tunnel and is heated as the wheel rotates. Another method uses several chambers containing inert ceramic materials with high heat retention capability. The hot gas (e.g. from the incinerator) passes through these beds and heats the ceramic material. The air flow is then reversed, and lower temperature gas passes through the heated beds; thus raising the temperature of that gas to rear incineration temperature. Further details on various heat recovery methods and equipment can be obtained from the vendors of incinerators.

The use of incinerator exhaust to preheat incinerator inlet air is often referred to as "primary" heat recovery as illustrated in Case 2 of Figure 3-13. Since some systems have a maximum allowable inlet temperature for the incinerator, it may not be possible to recover all of the heat available in the incinerator exhaust. In such case, the inlet to the incinerator is controlled to minimize fuel requirements. Note that a non-catalytic incinerator always requires some fuel to initiate combustion.

"Secondary" heat recovery uses incinerator exhaust from the primary heat recovery stage (or from the incinerator directly if there is no primary heat recovery) to replace energy usage elsewhere in the plant. This energy can be used for process heat requirements or for plant heating. The amount of energy that a plant can recover and use depends on the individual circumstances at the plant. Usually recovery efficiency of 70 to 80 percent is achievable, making the net energy consumption of an incinerator minimal or even negative if gases are near or above 25 percent of the LEL. The use of primary and secondary heat recovery is illustrated in Case 3 of Figure 3-13. It should be noted that heat recovery reduces operating expenses for fuel at the expense of increased capital costs. Primary heat recovery systems are within the incinerator and require no long ducts. Secondary heat recovery may be difficult to install on an existing process because the sites where recovered energy may be used are often distant from the incinerator. In applying calculated values for recovered energy values in Case 3 to real plants, the cost of using recovered energy must be considered. If secondary heat recovery is used, often the plant cannot operate unless the control system is operating because it supplies heat required by the plant.

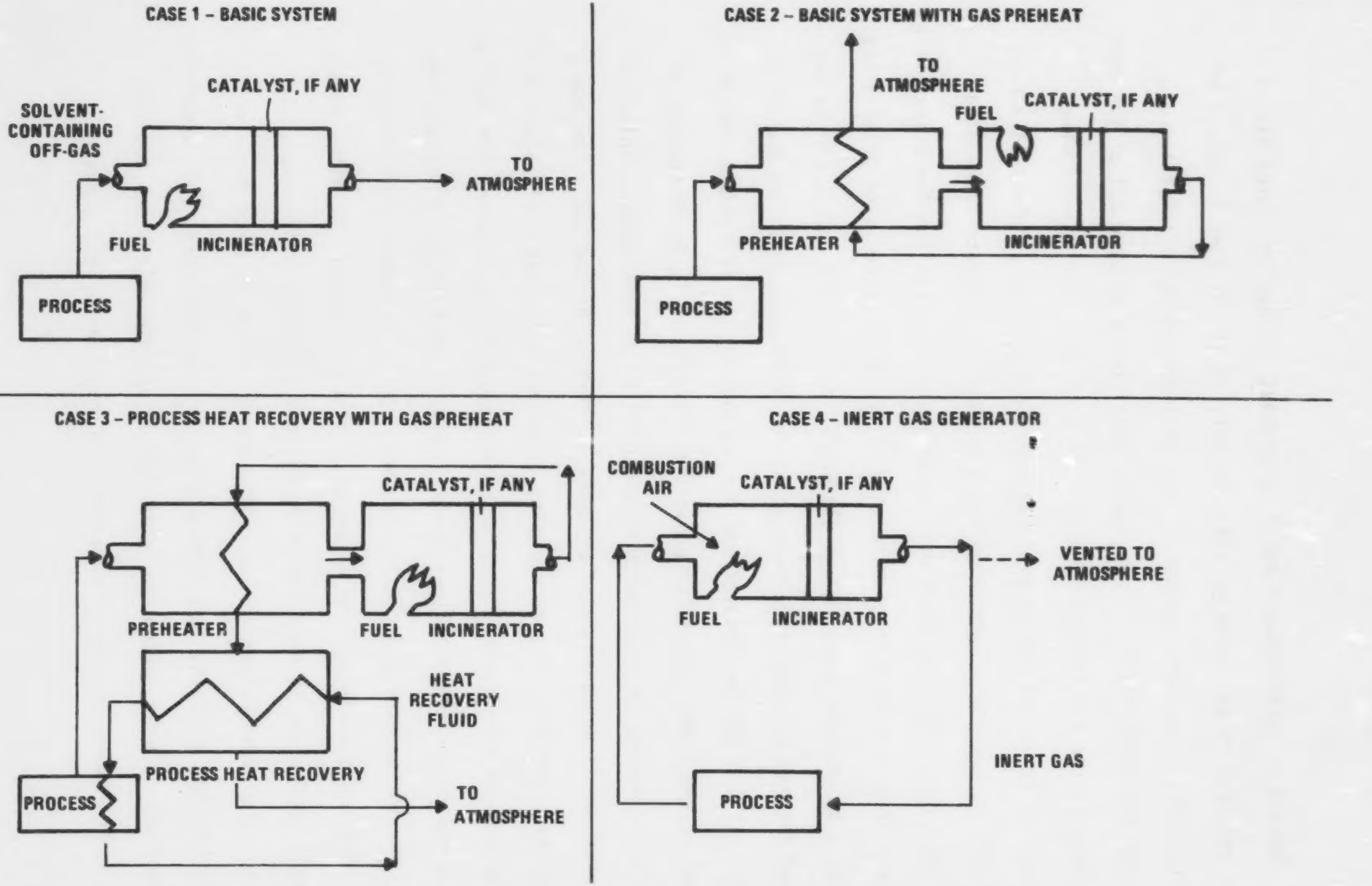
CASE 1 – BASIC SYSTEM
SOLVENT-CONTAINING OFF-GAS
CATALYST, IF ANY
TO ATMOSPHERE
FUEL
INCINERATOR
PROCESS
CASE 2 – BASIC SYSTEM WITH GAS PREHEAT
TO ATMOSPHERE
FUEL
CATALYST, IF ANY
PREHEATER
INCINERATOR
PROCESS
CASE 3 – PROCESS HEAT RECOVERY WITH GAS PREHEAT
CATALYST, IF ANY
PREHEATER
FUEL
INCINERATOR
HEAT RECOVERY FLUID
PROCESS HEAT RECOVERY
PROCESS
TO ATMOSPHERE
CASE 4 – INERT GAS GENERATOR
COMBUSTION AIR
CATALYST, IF ANY
VENTED TO ATMOSPHERE
FUEL
INCINERATOR
INERT GAS
PROCESS

Figure 3-13. Configurations for catalytic and noncatalytic incineration.

If the gases in an oven are inert, that is, contain little oxygen, explosions are not possible and high concentrations of organic solvent vapor can be handled safely. The oven exhaust can be blended with air and burned with minimal auxiliary fuel. The incinerator may be the source of inert gas for the oven. Cooling of the incinerator gas is necessary, removing energy that can be used elsewhere. Case 4 of Figure 3-13 illustrates this scheme. A modification of the scheme shown is the use of an external inert gas generator. This scheme can have a significant energy credit because the otherwise discarded organics are converted to useful energy. Because of the specialized nature of Case 4, it may not be applicable to retrofits on existing ovens and costs for this case are not included in this study. Note that in this case the incinerator exhaust is in contact with the product. This limits the available fuel for this option to natural gas or propane. The use of this option would probably be impossible if any compounds containing appreciable sulfur or halogens are used.

To illustrate a specific case, Figure 3-14 outlines a source controlled by a noncatalytic incinerator. The source is assumed to operate 25 percent of the LEL and the incinerator has primary and secondary heat recovery. The primary heat exchanger raises the temperature to 700°F, at 35 percent heat recovery efficiency. The heat of combustion of the organic vapors provides a 620°F additional temperature rise at 90 percent combustion and the burner must supply only enough heat to raise the gases 80°F to reach the design combustion temperature of 1400°F. Combustion products pass through the primary heat exchanger -- where

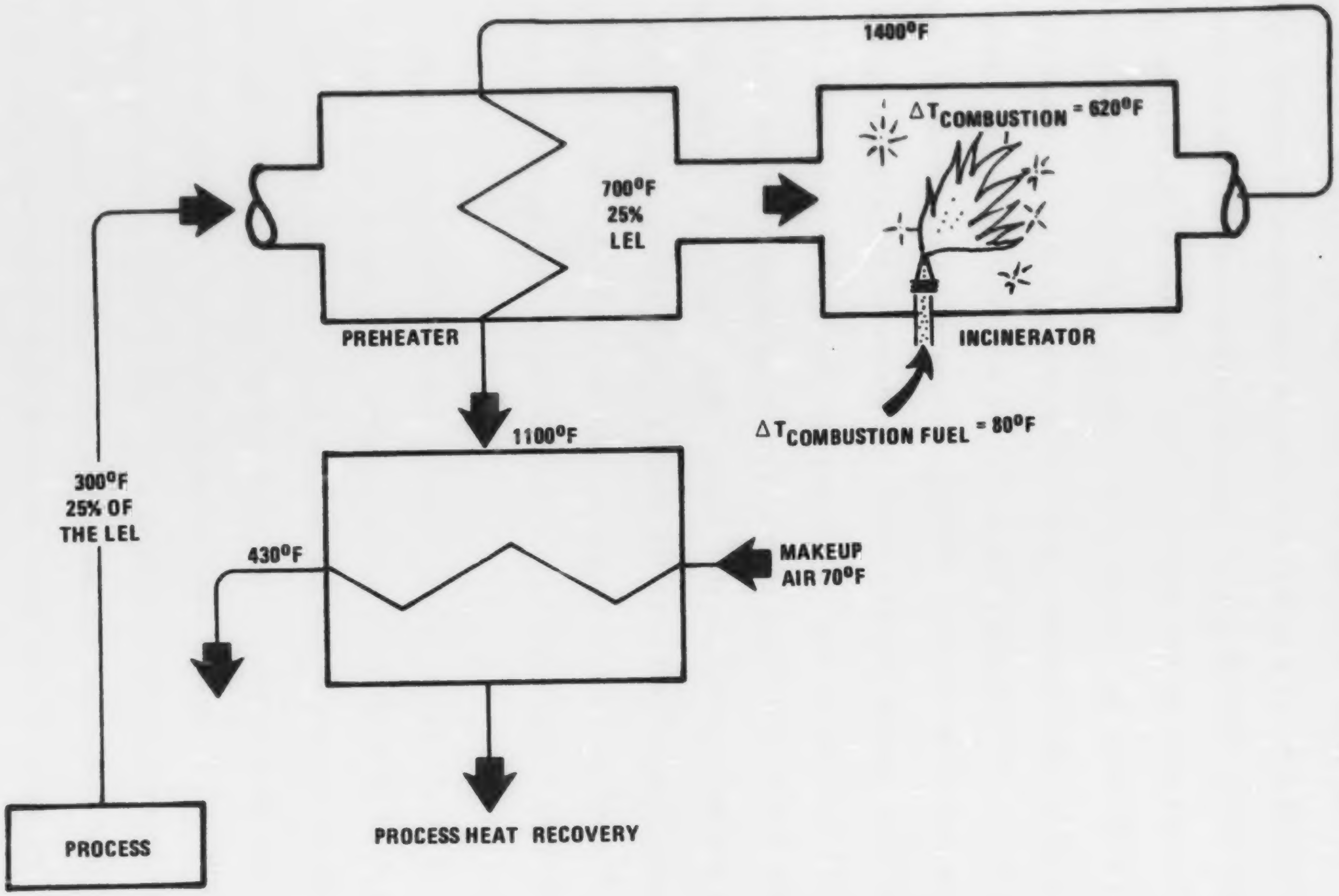
1400°F
ΔT COMBUSTION = 620°F
700°F
25%
LEL
PREHEATER
INCINERATOR
ΔT COMBUSTION FUEL = 80°F
1100°F
300°F
25% OF
THE LEL
430°F
MAKEUP
AIR 70°F
PROCESS
PROCESS HEAT RECOVERY

Figure 3-14. Example of incinerator on oven with primary and secondary heat recovery.

they are cooled to 1025°F -- and enter a 35 percent efficient secondary heat exchanger. In the secondary heat exchanger, further energy is recovered for use in other areas. In this example, makeup air for the source is heated from ambient temperatures to source entrance temperatures (higher than oven exit temperatures).

The energy implications of this scheme can be seen by comparing the energy input of this controlled source with an uncontrolled source. In an uncontrolled source, fuel would be necessary to raise the temperature of the makeup air from 70°F to 425°F or 355°F. For a controlled source, fuel would only need to raise the temperature 80°F. Thus, the energy input would be reduced by over 80 percent by use of incineration simply because the organic vapors contribute heat when they burn.

In the above analysis, the assumptions made are important. If the organic vapors are more dilute, the temperature rise due to combustion will be less. Heat recovery can be more efficient than 35 percent, making up for all or some of this difference. Finally, the analysis assumes that the heat recovered in the secondary heat exchanger can be used in the plant. The heat can be used to produce steam, heat water, supply process heat or heat buildings. Obviously, a case-by-case analysis is necessary to ascertain how much recovered heat could be used.

Particulates -- The level of particulate concentration found in surface coating operations should not pose any problems for noncatalytic volatile organic combustion. However, an incinerator designed for hydrocarbon removal usually will not have sufficient residence time to efficiently combust organic particulates.

Safety of preheat -- (At 25 percent of the LEL), oxidation rates at temperatures below 1100°F are slow. Complete oxidation can take several seconds. Because the gases are in the heat exchanger for less than a second preignition should not be a problem using heat recovery if temperatures are below 1000°F to 1100°F.

Some problems have occurred in the past with accumulations of condensed materials or particulates igniting in the heat recovery devices. If this occurs, the accumluations must be periodically removed from the heat transfer surfaces. The user should give careful consideration for his particular set of circumstances to potential safety problems. This is especially true if gases at a high percent of the LEL are preheated.

Adverse environmental effects -- Sulfur-containing compounds will be converted to their oxides; halogen-containing compounds will be converted to acids. A portion of nitrogen-containing compounds will be converted to NO_x and additional NO_x will result from thermal fixation. If use of these compounds cannot be avoided, the benefit from incineration should be evaluated against the adverse effects and alternate methods of control should be thoroughly explored.

The concentration of oxides of nitrogen (NO_x) is about 18 to 22 ppm for natural gas-fired noncatalytic incinerators and 40 to 50 ppm for oil-fired noncatalytic incinerators at a temperature of 1500°F, assuming no nitrogen containing compounds are incinerated.

Effect of Technical Assumptions on Cost Models -- In the cost estimates (Section 4.2.2.1) for noncatalytic incineration, the organic was assumed to be 50 molar percent hexane and 50 molar percent benzene. For noncatalytic incineration, the two important factors are the heat available per unit volume at the LEL and the temperature necessary for combustion. For most solvents, the heat of combustion at the LEL is about 50 Btu/scf.[2] This will vary about ± 20 percent for almost the entire range of solvents used (methanol and ethanol are slightly higher). Thus, there is little variation due to the type of solvent.

The assumed temperature of combustion (1400°F) is sufficient to obtain 95+ percent removal of the entire range of organics used as solvents.

3.2.2.2 Catalytic Incineration -- A catalyst is a substance that speeds up the rate of chemical reaction at a given temperature without being permanently altered. The use of a catalyst in an incinerator reportedly enables satisfactory oxidation rates at temperatures in the range of 500 to 600°F inlet and 750 to 1000°F outlet. If heat recovery is not practiced, significant energy savings are possible by use of a catalyst. The fuel savings become less as primary and secondary heat recovery are added. Because of lower temperatures, materials of construction savings are possible for heat recovery and for the incinerator itself. A schematic of one possible configuration is shown in Figure 3-15.

Catalysts are specific in the types of reactions they promote. There are, however, oxidation catalysts available that will work on a wide range of organic solvents. The effect of temperature on conversion for solvent hydrocarbons is shown in Figure 3-16. Common catalysts are platinum or other metals on alumina pellet support or on a honeycomb support. All-metal catalysts can also be used.

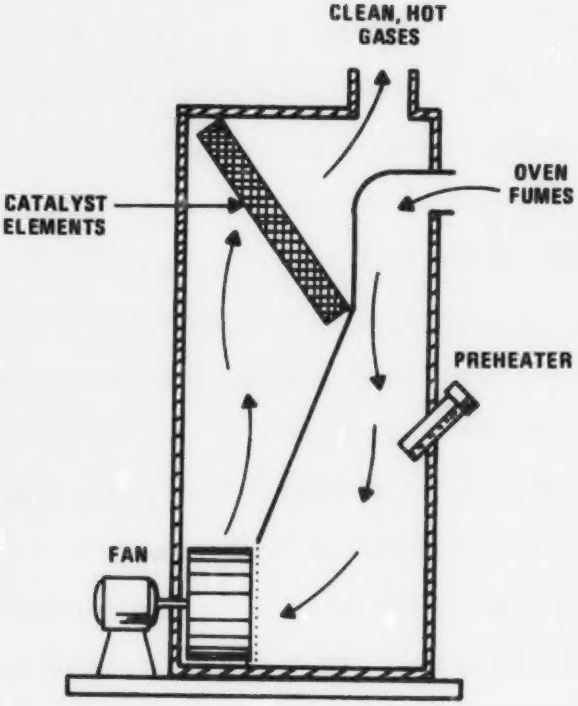
CLEAN, HOT GASES
OVEN FUMES
CATALYST ELEMENTS
PREHEATER
FAN

Figure 3-15. Schematic diagram of catalytic afterburner using torch-type preheat burner with flow of preheater waste stream through fan to promote mixing.[1]

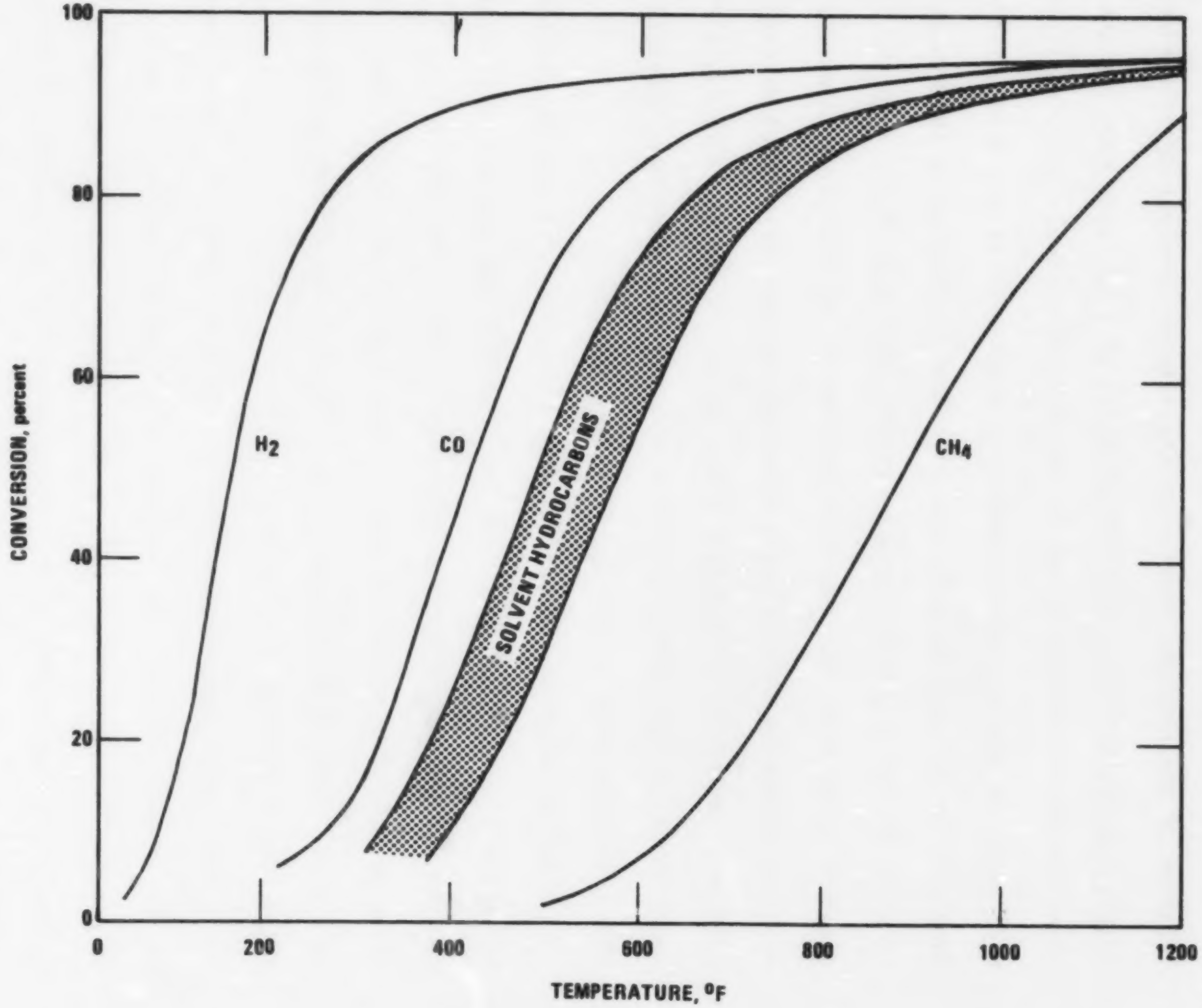

Figure 3-16. Effect of temperature on conversion for catalytic incineration.[1]

The initial cost of the catalyst and its periodic replacement represents, respectively, increased capital and operating costs. The lifetime of the catalyst depends on the rate of catalyst deactivation.

Catalyst Deactivation -- The effectiveness of a catalyst requires the accessability of "active sites" to reacting molecules. Every catalyst will begin to lose its effectiveness as soon as it is put into service. Compensation for this must be made by either overdesigning the amount of catalyst in the original charge or raising the temperature into the catalyst to maintain the required efficiency. At some time, however, activity decays to a point where the catalyst must be cleaned or replaced. Catalysts can be deactivated by normal aging, by use at excessively high temperature, by coating with particulates, or by poisoning. Catalyst lifetime of greater than 1 year is considered acceptable.

Catalyst material can be lost from the support by erosion, attrition, or vaporization. These processes increase with temperature. For metals on alumina, if the temperature is less than 1100°F, life will be 3 to 5 years if no deactivation mechanisms are present. At 1250 to 1300°F, this drops to 1 year. Even short-term exposure to 1400 to 1500°F can result in near total loss of catalytic activity.[1]

The limited temperature range allowable for catalysts sets constraints on the system. As mentioned earlier, at 25 percent of the LEL and 90 percent combustion there will be about a 620°F temperature rise as a result of organic combustion. Because an inlet temperature of 500 to 600°F is necessary to initiate combustion, the catalyst bed exit temperature will be 1120 to 1220°F at 25 percent of the LEL. This is the upper limit for good catalyst life and thus concentrations of greater than 25 percent of the LEL cannot be incinerated in a catalytic incinerator without damage to the catalyst. Restrictions on heat recovery options are also mandated. These will be discussed later.

Coating with particulates -- The buildup of condensed polymerized material or solid particulate can inhibit contact between the active sites of the catalyst and the gases to be controlled. Cleaning is the usual method for reactivation. Cleaning methods vary with the catalyst and instructions are usually given by the manufacturer.

Poisoning -- Certain contaminants will chemically react or alloy with common catalysts and cause deactivation. A common list includes phosphorus, bismuth, arsenic, antimony, mercury, lead, zinc, and tin. The first five are considered fast acting; the last three are slow acting, especially below 1100°F. Areas of care include avoiding the use of phosphate metal cleaning compounds and galvanized ductwork. Sulfur and halogens are also considered catalyst poisons, but their effect is reversible.

Fuel -- Natural gas is the preferred fuel for catalytic incinerators because of its cleanliness. If properly designed and operated, a catalytic incinerator could possibly use distillate oil. However, much of the sulfur in the oil would probably be oxidized to SO_3 which would subsequently form sulfuric acid mist. This would necessitate corrosive resistant materials and would cause the emission of a very undesirable pollutant. Therefore, the use of fuel oil (even low sulfur) in a catalytic incinerator is not recommended.

Heat Recovery -- The amount of heat that can be transferred to the cooler gases is limited. The usual design is to have the exit temperature from the catalyst bed at about 1000°F. If the gas is at 15 percent of the LEL, for example, the temperature rise across the bed would be about 375°F, and the gas could only be preheated to about 625°F. Secondary heat recovery is limited by the ability to use the recovered energy. If a gas stream is already at combustion temperature, it is not useful to use "primary" heat recovery but "secondary" heat recovery may still be possible. Note that for catalytic incineration, no flame initiation is necessary and thus it is possible to have no fuel input.

As in noncatalytic systems, heat recovery equipment may need periodic cleaning if certain streams are to be processed. For a discussion of the safety of preheat, see Section 3.2.2.2.

Adverse environmental effects of catalytic incineration -- As in noncatalytic incineration, if sulfur- or nitrogen-containing compounds are present, their oxides will be generated. If halogenated compounds are present, their acids will be formed. If it is impossible to avoid using these compounds in quantity, incineration may be unwise.

The concentration of NO_x from catalytic incinerators is low, about 15 parts per million,[2] assuming no nitrogen compounds are incinerated.

Effect of technical assumptions on cost models -- In the cost estimates for catalytic incineration, the solvent was assumed to be 50 molar percent hexane and 50 molar percent benzene. For catalytic incineration, the two important factors are the heat available per unit volume at the LEL and the temperature necessary for catalytic oxidation.

As discussed earlier, there is little variation in the available heat from combustion at the LEL.

The assumed temperature into the catalytic incinerator is sufficient to obtain 95 percent removal of the entire range of organics used in solvents.

3.2.3 Condensation

Any component of any vapor mixture can be condensed if brought to equilibrium at a low enough temperature. The temperature necessary to achieve a given solvent vapor concentration is dependent on the vapor pressures of the compounds.

When cooling a two-component vapor where one component can be considered noncondensible, for example, a solvent-air mixture, condensation will begin when a temperature is reached such that the vapor pressure of the volatile component is equal to its partial pressure. The point where condensation first occurs is called the dew point. As the vapor is cooled further, condensation continues such that the partial pressure stays equal to the vapor pressure. The less volatile a compound, that is, the higher the normal boiling point, the lower will be the amount that can remain vapor at a given temperature.

In cases where the solvent vapor concentration is high, for example, from the desorption cycle of a carbon adsorber, condensation is relatively easy. However, for sources where concentrations are typically below 25 percent of the LEL, condensation is very difficult.

Nonhalogenated organic vapors at 25 percent of the LEL or less are already very dilute, that is, on the order of 0.15 to 2 percent by volume. Figure 3-17 shows the vapor pressure dependence on temperature for several compounds. Table 3-3 shows the temperature necessary to condense various amounts of compounds spanning the volatility range of compounds used for solvents. Note that dodecane is not volatile enough to be used as a major component in most solvents. To cool large quantities of gas from ambient or oven temperatures to below 0°F would be economically prohibitive.

The above calculations are for single condensable compound systems. The calculation methods for multiple condensable component systems are complex, particularly if there are significant departures from ideal behavior of the gases and liquids. As a simplification, the temperatures necessary for control by condensation can be roughly approximated by the weighted average of the temperatures necessary for condensation of a single condensable component system at concentrations equal to the total organic concentration.

Totally chlorinated and fluorinated compounds, for example, carbon tetrachloride and perchlorethylene, are nonflammable and may be handled safely in all concentrations for nonoccupied areas. Condensation may be practical if high concentrations of these solvents are present. In fact, condensation is widely used in the drycleaning industry for perchloroethylene recovery, because the relatively high cost of chlorinated solvents makes recovery attractive. Totally chlorinated compounds, however, are not used extensively in the surface coating industry.

TABLE 3-3. PHYSICAL CONSTANTS AND CONDENSATION PROPERTIES OF SOME ORGANIC SOLVENTS

			25% of LEL concentration		90% condensation from 25% of LEL		95% condensation from 25% of LEL		90% condensation from 200 ppm	
Compound	Normal boiling point, °F	(a) LEL, %	Partial pressure, mm of Hg	Dew point, °F	Partial pressure, mm of Hg	(b) Temp, °F	Partial pressure, mm of Hg	(b) Temp, °F	Partial pressure, mm of Hg	(b) Temp, °F
Dodecane	421	0.6	1.1	120	0.11	61	0.55	54.4	0.15	19
Pinene $C_{10}H_{16}$ (Terpentine)	300	0.7	1.3	53	0.13	116	0.065	-31.4	0.015	-60
O-xylene C_8H_{10}	280	1.0	1.9	26	0.19	-31	0.095	-36.5	0.015	-72
Toluene C_7H_8	211	1.4	2.7	5	0.27	-51	0.135	-54.3	0.015	-103
Benzene	175	1.3	2.5	-15	0.25	-69	0.125	-96.4	0.015	-114
Methanol C_2H_6O	147	6.0	11.4	2	1.14	-41	0.57	-68.7	0.015	-126
Hexane C_6H_{14}	155	1.2	2.3	-39	0.23	-93	0.115	-108	0.015	-129

(a) From Reference 1

(b) From Figure 3-16

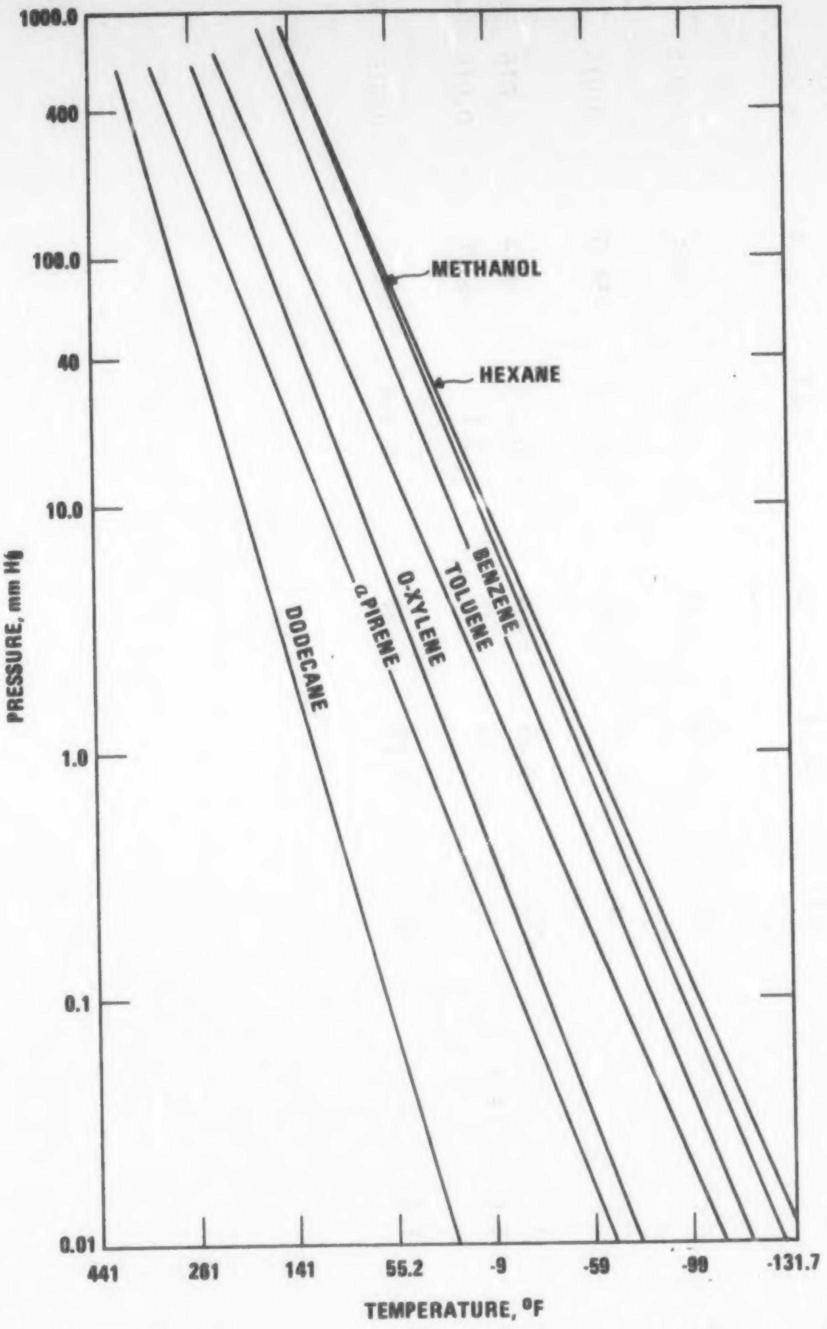

Figure 3-17. Vapor pressures of organic solvents versus temperature.

In summary, condensation is not applicable as an organic solvent control method for surface coating except in rare instances in which high concentrations of relatively nonflammable materials are present.

3.2.4 Absorption (Scrubbing)

Absorption, as an air pollution control process, involves dissolving a soluble gas component in a relatively nonvolatile liquid. The absorption step is only the collection step. After the gas is dissolved, it must be recovered or reacted to an innocous form.

Common absorbents for organic vapors are water, nonvolatile organics, and aqueous solutions.[3] Absorption is increased by lower temperatures, higher solubility of the gas, higher concentrations of the gas, higher liquid to gas ratios, lower concentrations of gas in the liquid, and greater contacting surface. Absorption has been widely used as a product recovery step in the petroleum and petrochemical industry where concentrations are typically very high. These products are generally recovered by heating to lower the solubility, or by distillation.

If the chemical oxidizer is present in the liquid stream, organics can be oxidized in the stream. This technique has been used to convert low concentrations of odorous compounds to less odorous forms. The expense of the oxidizing chemical, however, prevents its use where concentrations greater than a few parts per million are present.

The absorption-regeneration approach for organic solvents is severely limited by the low concentrations and consequent low solubilities of most organic gases in the absorbent. Exceptions are alcohols, ketones, amines, glycols, aldehydes, phenol, and organic acids. Gases may be regenerated by heating and reclaimed by condensation or destroyed by incineration.

Direct contact with water may be used as a cooling method for removal of high boiling compounds to avoid opacity problems in the exhaust or to preclean the air before a carbon absorber, but in most cases the materials do not go into solution to any appreciable extent. If water is used for condensation in this way, water treatment may be necessary before discharge.

In summary, except for a few specialized cases, absorption is not applicable to control of organic solvent emissions from surface coating except as a preliminary step for particulate and high-boiling compound removal.

3.3 PROCESS AND MATERIAL CHANGES

3.3.1 Water-borne Coatings

3.3.1.1 Introduction -- There is much confusion over the terminology of coatings containing water as part of their solvent content. Water-borne, water-reducible, water-based, water-thinnable, and latex are all used to describe these coatings. Strictly speaking, water-borne is the correct generic term for coatings containing water.[4] The base of a coating is the polymer or resin, but many use the term water-based interchangeably with water-borne.

There are three types of water-borne coatings: water-solutions, water-emulsions, and water-dispersions. Water-solution coatings feature very small particles dissolved in a mixture of water and a coupling solvent.[5] The water-soluble resins normally contain ionizable amine or carboxylic acid groups that solubilize the molecules.[4] These systems are more easily mixed and applied than other water-borne systems. However, resin properties that make the resin soluble can also cause water sensitivity after curing unless additions are made to eliminate this sensitivity.

Water-emulsions are high molecular weight particles suspended in water by some stabilizing, dispersing agent.[5] The resins, of which vinyls and acrylics are the most prominent, have very few functional groups and require emulsifying agents to maintain their form.[4] Emulsion coatings generally have the highest water resistance of the water-borne systems.

Water dispersion coatings are intermediate in particle size, in use of functional groups, and in water sensitivity.

3.3.1.2 Application Techniques -- Water-borne coatings may be applied using any of the methods used for organic solvent-borne coatings, that is, knife, blade, roller, dip, flow coat, and spray. The conductivity of water also enables use of electrophoresics to deposit a coating on conductive materials. Conversely, the conductivity makes electrostatic spray more difficult, although still feasible. Also, a new dip process is available in which the driving forces are chemical rather than electrical in nature.[6,7]

Knife and roller coatings -- Application of water-borne coatings with a knife or roller presents no special problems. Corrosion-resistant vessels and delivery lines must be used as for all water-borne paint facilities. Small amounts of grease or soot that would be no problem with organic solvent-borne coatings may produce unacceptable coverage with water-borne coatings. Therefore, for knife and roller coating and for all other water-borne applicaitons, surface cleanliness is vital.

Dipping -- Dipping of materials in water-borne paints has many forms. A dip into a bath of water-borne coating may be applicable for a material that does not need a smooth surface. This method has been used for parts of automobiles that are not usually visible after assembly.

Electrophoretic coating -- By using a direct current potential in a bath and grounding the item to be coated, the item can act as an anode or cathode and be coated. This method was first used by Ford Motor Company in the early sixties.[5] It is now a proven method for primer application in the automotive industry[8] and is finding use in single coat metal finishing applications.

This method is applicable for conductive surfaces and non-conductive surfaces that can be rendered conductive. A very even coat is produced, and coverage of edges and hidden parts is excellent. The system has been applied to prime trucks, automobiles, appliances, and other metal objects.

Because the item is immersed, care must be taken to avoid contamination of the bath since the bath is very susceptible to impurities. Washing with deionized water is necessary before immersion in a dip tank for 1 to 3 minutes. The thickness of the coating may be adjusted by the voltage and to a lesser extent by the immersion time. The composition of the bath fluid is usually 10 to 15 percent solids, 80 to 85 percent water, and 5 percent organic solvent. The composition of the coating as it emerges from the system is usually above 75 percent solids, and less than 23.5 percent water and 1.5 percent organic solvent.

The tank must be continuously agitated, filtered, temperature-, pH-, and bath solids-controlled to give proper coating. Cooling must be supplied to overcome the effects of electrical heating.

Upon exiting the system, the item must be rinsed to remove excess coating. Ultrafiltration is used to recover paint solids from the rinse water. The solids are returned to the tank and the pure ultrafiltrate water is used to supplement the deionized water that is normally used for the final rinse.

Control of the system is complex but largely automated. One operator normally monitors the equipment and performs analyses on the bath. The operator does not enter the bath area, and hence ventilation of the tank is minimal. During an annual tank cleaning, a spare tank is used to hold the coating.

The electrodeposition system is a signficiant user of electrical energy. For the General Motors plant at Framingham, Massachusetts, the device operates at 1000 amps and 400 volts. Each automobile is in the tank for about 3 minutes; thus, electrical energy usage is about 20 kw/hr per automobile. In addition, a 150-ton cooling system is required to maintain the bath temperature. This overall energy usage must be balanced against tne energy usage for ventilation and particulate collection in a spray booth.

A significant drawback for these systems is their high investment cost. The systems are limited to one color per bath and this would be prohibitive for final coat where many colors were needed. Lack of gloss is also a drawback for topcoat application.

Energy to cure water-borne coatings is considerably higher than that necessary to cure solvent-borne coatings. This will be discussed later.

Autodeposited coatings -- A truck plant has recently installed an "autodeposited" priming system for frames.[6,7] This plant has been reported to have now completed 11 months of successful production. Another company has recently started operation of a autodeposition line for head light housings. A third line is scheduled to start operation very soon.

The exact details of the process are proprietary, but it is claimed that is achieves the same result as electrodeposition without the electrical requirements. The process is claimed to now be past the developmental stage. Current problems include inability to coat items of more than one metal (such as carbodies) and the nonsandability of the coatings.[9]

Flow coating -- Flow coating is simply the immersion of an item in a coarse spray of coating material. Most of the coating runs off the item and is recirculated. The coating is neither even nor smooth enough for visible areas unless sanding is performed on edges.

Spray coating -- Water-borne coatings may be applied by air spray, airless spray, and electrostatic spray. Observance of safety considerations with the high voltage make manual electrostatic spray possible.

The main problems with spraying of water borne coatings arise from the physical nature of the solvent. Organic solvents for coatings are usually a mixture of several components. Some solvent evaporates while the spray is in transit from the gun to the object. Some evaporates very quickly to obtain the viscosity necessary to avoid dripping while allowing leveling. The remainder has a higher boiling point and comes out slowly to allow leveling of the coating and to avoid bubbles from forming due to too rapid escape of solvent. Because there is originally no organic solvent in incoming air, these evaporation properties are not dependent on the properties of the incoming air (other than temperature).

Water-borne spray coating solvent is typically 70 to 80 percent water and 20 to 30 percent organic solvent. The organic solvent is a necessary part of the coating that gives proper leveling and performance properties. Unlike organic solvent mixtures, water is only one compound with one evaporation rate and boiling point. The heat of vaporization is much higher than organic solvents and the rate of evaporation from a coating is very dependent on the relative humidity of the air surrounding the coating as well as the cosolvents used. Roller application followed immediately by curing has little humidity problem. When spray coating with water-borne coatings, humidity control is required. This increases energy consumption. This is an especially severe problem when spray booths are occupied.

3.3.1.3 Performance and Appearance -- Appearance of water-borne enamels can be as good as organic solvent-borne enamels if proper curing procedures are used. "Orange peel," that is, bumpiness of the surface, is greater for any enamel than for lacquer. The organic solvent portion of water-borne coatings minimizes this "orange peel" effect. Only a limited number of resins are available that allow the generation of high-gloss water-borne coatings. Water-borne coatings for aluminum are farthest advanced with tin-plate steel second. Coaters producing a wide variety of products and coaters who must warrant products for long periods of time in severe environments have the same problems with water-borne coatings as they do with other process changes.

3.3.1.4 Energy Consumption -- The energy required to remove the solvent is greater for a given amount of water than for the same amount of organic solvent. The heat of vaporization of water is about 1000 Btu/lb, about

5 times that for most organic solvents. The curing temperatures and time for water-borne coatings is greater than for organic solvent-borne coatings. It should be noted that the energy for heating the part itself often exceeds the energy to remove the solvent and cure the coating, particularly with large metal parts. Counterbalancing these higher energy items is a significant savings in oven air heating costs. Air recirculation is governed by the necessity to maintain levels below 25 percent LEL (or somewhat greater with proper safety controls). Because of the lower solvent content per unit weight of solids, the volume of exhaust air can be safely reduced somewhat. In some cases, however, the coating quality can be adversely affected by too large a reduction, because of the drying properties of the coating. The net result is that the energy required to cure water-borne coatings is approximately equal to that for organic solvent-borne coatings for some applications but will be somewhat higher for most applications.

If humidity control is required, a significant increase in electrical energy will occur, especially if the coating is applied in an occupied area. This will be discussed for the automotive and light truck assembly industry in Volume II.

3.3.1.5 Safety -- One of the major advantages of water-borne coatings is their non-flammability and low toxicity. Considerable savings in insurance costs can be realized in some cases.

3.3.2 High-solids Coatings

3.3.2.1 Introduction -- The basic ingredient in an organic coating is the binder or resin. A resin is a film-forming organic polymer having glassy, plastic, or rubbery properties in the dried state. As applied the resins are liquids of controlled viscosity. On drying and curing (baking) the materials undergo polymerization and cross-linkage to form a solid film of the desired properties.

The materials for resins to be used in conventional solvent-borne coatings are "cooked" in resin kettles to yield liquids which have a high viscosity at ambient temperatures. To facilitate compounding with pigments the resins are dissolved in organic solvents which reduce the viscosity. To facilitate application more solvent may be added. After application, the solvent evaporates and the resins further polymerize to yield the solid film.

The viscosity of the coating as applied can be reduced by using low molecular weight monomers or "prepolymers," which are applied and then polymerized (cured) to the high molecular weight solid film. The amount of solvent required decreases with decreasing reactant molecular weight. However, as the molecular weight of the resin formers are reduced, the difficulty of controlling the polymerization reactions increases. The application and curing conditions must be precisely fitted to the reactant characteristics to yield a film of the desired properties.

Another method of reducing viscosity of high-solids coatings is by heating the coating material. As a rule of thumb an increase in temperature from 70°F to 125°F is equivalent to a 10 percent solvent reduction. However, heating can cause loss of solvent crucial to the application performance of high-solids coatings. Heating can also cause premature gelation of coatings, particularly on standing.

The solids content of a coating is expressed as the volume or weight of the final cured coating per volume or weight of the coating as applied. The term "high solids coatings" is usually reserved for low solvent coatings which are applied and cured by conventional means. Low molecular weight materials which are cured by radiation (ultraviolet, infrared, and electron beam) are classified separately. Radiation-cured coatings are discussed in Sections 3.3.3 and 3.3.8.

High solids coatings were first defined by the Los Angeles County Air Pollution Control District in its Rule 66; coatings of 80 percent or more solids (by volume) were exempt from emission limitations.

Segments of the coatings industry have asked regulatory agencies to accept 70 percent solids by volume as the definition of high solids. Because the viscosity of a coating increases rapidly with solids content, coating manufacturers reported that serious coating application problems are encountered at 80 percent solids content. As a consequence, some regulations have been adopted that give exemptions to coatings with 70 percent solids by volume. The Boston Transportation Control Plan[10] is one such regulation.

Some coatings industry representatives also report that even coatings of 70 percent solids by volume are not now technologically feasible, although they consider 70 percent solids by weight as reasonable. Seventy percent solids by weight corresponds to 54 to 65 percent solids by volume depending on the coating compostion. Representatives from the state agencies of 19 northeastern states (referred to as the Moodus Conference) on September 28, 1976, in New York City recommended that coatings with 70 percent solids by weight and coatings whose liquid fraction contains no more than 30 percent volatile organic compounds be allowed emission limits of 550 lbs per day and 110 lbs per hour.

3.3.2.2 Materials and Processes -- Most high solids resins fall into two categories, two component ambient temperature cured and single component heat converted. The most important types are as follows:

Two Component Ambient Cure	Single Component Heat Converted
Urethane	Epoxy
Acrylic-Urethane	Acrylic
Epoxy/amine	Polyester
	Alkyd

Many two component systems use a catalyst to increase the curing reactions. Although these chemical reactions can take place at room temperature, many plants use low-temperature ovens to cure two-component systems rapidly so that the coated product can be handled sooner. The oven temperatures required are much lower than for conventional ovens and the amount of solvent is lower. This will result in large energy savings. Most thermosetting high-solids coatings are based on epoxy or urethane resins. The most popular two-component coatings are based on polyurethane resins. Coatings properties compare favorably with those obtained from conventional based enamels. Toxicity of the isocyanates used for urethanes is a potential problem.

Fast-reacting two-component systems are usually applied with special spray guns that mix the two components at the spray nozzle. This equipment, more complicated than conventional spray equipment, is also more expensive. Some slower-reacting two-component coatings can be applied with conventional spray equipment.

High-solids coatings can be used in a variety of industrial coating processes. Two-component catalytically cured coatings are presently being air sprayed to coat small metal products. It might be possible to coat larger products such as automobiles with such systems. The coil coating industry is currently investigating the possibility of using high-solids coatings, especially two-component coatings.[11] The can industry is testing a roll-coat-applied high solids coating for can exteriors. Interiors of cans can possibly be coated with spray-applied high-solids coatings. Coatings of high viscosity can be applied with a knife coater, therefore, the paper and cloth industry may be able to apply high-solids coatings using existing knife coating equipment.

3.3.2.3 Advantages of High-solids Coatings -- In addition to reduction of solvent emissions high-solids coatings have other advantages:

1. In most cases conventional application methods can be used. Therefore, conversion costs are low.

2. In many cases, the energy required for curing is less than either conventional solvent coatings or water-borne coatings. However, in some cases higher curing temperatures are required and energy usage is greater than for conventional coatings.

3. In some cases thick coatings can be applied, that mask surface defects (if desired), so that less surface preparation for a product is needed.

3.3.2.4 Disadvantages of High-solids Coatings -- The limitations of high-solids relate to the properties and availability of these coatings:

1. Achieving the desired properties in the finished coating is difficult. In conventional coatings the necessary functional properties are created by polymer building in the resin kettle. Solvents are then added to optimize application and appearance. Most of the polymerization in high-solids coatings occurs after application and controlling the conditions so as to produce the desired properties is much more difficult.

2. The availability of high-solids coatings is very limited. These coatings are just beginning to be converted from laboratory coatings to proven industrial finishing systems. Coating manufacturers report that efforts to produce coatings of 80 percent solids by volume have been unsuccessful. Coatings of 70 percent solids are still in the developmental stage. Only coatings in the 50 to 60 percent solids range appear to offer immediate prospects for expansion to widespread usage.

3. Pot-life of two component systems is very short, leading to application difficulties.

4. There is a health hazard associated with the isocyanates used in some two-component systems (urethanes).

3.3.2.5 Organic Solvent Emission Reduction Potential -- In order to compare emissions for coatings of various formulations a common basis is necessary, such as a given volume or weight of cured solids. Table 3-4 makes such a comparison for organic solvent-borne coatings and water-borne coatings. The water-borne coating is assumed to have a volatile portion containing 80 percent water and 20 percent organic solvent. Such coatings are exempt from emission limitations by Rule 66 type regulations.

It can be noted that the emissions from a typical water-borne coating of 25 percent solids by volume will have about the same emission as an organic solvent-borne coating of 60 percent solids by volume. Coatings manufacturers and users have contended that organic solvent-borne coatings should have the same emission exemption as water-borne coatings, on the basis of comparable quantities of solids. They maintain that such an allowance would greatly stimulate the further development of high-solids coatings.

3.3.3 Powder Coatings

3.3.3.1 Introduction -- Powder coating involves the application of finely divided coating solids to a surface, followed by a melting of the coating solids into a continuous film. Very little solvent is used (less than one percent), and the process is thus almost pollution free. Several types of resins may be applied as a powder, but there are limitations on the type of objects that can be powder coated. Advantages of and problems with powder coating are discussed below.

TABLE 3-4. COMPARISON OF EMISSIONS FROM ORGANIC SOLVENT-BORNE AND WATER-BORNE COATINGS

Basis: 1 gal of solids weighing 11 lbs.

Organic Solvent-Borne Coating		Organic Emissions	
Percent Solids			
by Vol	by Wt.	gal	lbs
12	20.5	7.3	42
20	29.7	4.0	26
30	41.7	2.3	15
40	52.7	1.5	9.9
50	62.5	1.0	6.6
60	72.0	0.67	4.3
70	79.7	0.43	2.8
80	86.8	0.25	1.6

Water-borne* Coatings		Organic Emissions	
Percent Solids			
by Vol	by Wt.	gal	lbs
10	13.3	1.8	11.9
15	19.6	1.1	7.4
20	26.2	0.8	5.3
25	31.4	0.6	4.0
30	36.9	0.5	3.1
35	42.7	0.37	2.4

*Volatile portion is assumed to be 80 percent water and 20 percent organic solvent.

3.3.3.2 Advantages of Powder Coating -- In addition to the almost total elimination of organic solvent emissions, powder coating has several advantages over solvent-borne coating:

1. Single coat application is possible with the fluidized bed technique for thickness up to 40 mil with one application versus several applications necessary for solvent-borne coatings.

2. Material utilization can approach 100 percent if the powder can be collected and reused. This factor allows powder coating to be potentially the most economical coating material. The difficulty with reuse of powder occurs if multiple colors are used. This will be discussed later.

3. Safety aspects of powder coatings offer some advantages. Powders are low in toxicity and nonflammable in storage; however, virtually any organic powder suspended in air can be explosive.

4. Maintenance is generally less because the powder can be vacuumed from any unbaked areas. Likewise the paint from any mistakes can simply be vacuumed off from unbaked items.

5. Exhaust air volume is greatly reduced from that used for solvent-borne spray because application is generally either automatic or else done in a much smaller area. Spray booth air theoretically could be filtered and returned to the plant interior. Fan power is reduced as are space cooling or heating requirements.

6. Water pollution problems are absent because dry particulate collection is possible.

7. Natural gas usage can be theoretically decreased because little dilution air is required in ovens. However, higher bake temperatures are usually required, which may result in increased gas usage.

3.3.3.3 Disadvantages of Powder Coating -- Some of the specific problems with different methods of application are discussed later. General problem areas include the following:

1. Color change is a difficult problem for powder. The automobile and truck assembly industry has this problem in its extreme. Here, color changes can occur as often as once a minute and with as little as 15 seconds to change colors between vehicles. Furthermore, more than a dozen colors are usually applied. For fluidized bed methods, considerable time would be necessary to switch colors because cleanout of the equipment would be necessary. A separate dip for each color would be necessary if color were changed more than once a day. For spray operations, the problem of changing colors can be solved by switching coating supply lines and purging the small amount of powder in the nozzle. This can, however, be a difficult mechanical problem. A remaining difficulty with color change is the problem of reusing overspray. If colors become mixed in the collection device, reuse of powder is impossible for any applications that change colors more than about once a day, unless the number of colors are few and it is feasible to use separate spray areas for each. Without the ability to reuse the oversprayed powder, powder coating loses one of its chief economic advantages--- low materials loss.

2. Color masking is more difficult for electrostatically applied powder coatings than for solvent-borne coatings. Fine detail, such as printing, is not possible and even two-tone automobiles present a problem, albeit a solvable one.

3. Powder coating materials are discrete particles each of which must be the same color. Thus, there can be no user tinting or blending and all colors must be available from the manufacturer. For a coater that must match a given color, such as in a trademark, the necessary color may not be available. Color matching problems can occur when using recycled powder.

4. The high curing temperature required for powder coatings makes them applicable only for metals and some plastics.

5. A typical particle size for sprayed powder coating materials is generally greater than 15 micrometers.[12] Because 1 mil is about 25 micrometers, it is obvious that thin, uniform spray coatings are difficult to achieve at coating thickness of less than 2 to 3 mils. Fluidized bed coating materials are usually about 200 micrometers in diameter and thus are not applicable for thin coatings.

3.3.3.4 Application Methods -- The three general application methods for powder coatings are electrostatic spray, conventional fluidized bed, and electrostatic fluidized bed.[12]

Electrostatic Spray -- In this method, an electrostatic charge is used to attract and hold the particles to the object until they can be heated to form a continuous coating. Electrostatic powder spray coating involves the passing of a powder through a spray gun where it is given an electrical charge. The object is electrically grounded and the powder is attracted to the object. If the object is above the melting point of the powder, the powder will melt, losing most of its charge and allowing further attraction. If the object is not above the melting point, the powder will be attracted to the surface and the charge will build up because unmelted powder is generally a poor electrical conductor. The powder is attracted to areas with less coating and thus good uniformity of coating is obtained. Powder continues to build up until the charge from deposited powders is such that no more powder is attracted. The applied powder will remain attracted to the object until the powder is melted into a continuous, smooth coating. Application can be automatic or by manual spray. An example of an electrostatic spray line is shown in Figure 3-18.

In electrostatic spray application, the object to be coated does not need to be hot and thus does not need to have a high heat capacity. There is, however, the requirement that the surface be conductive so that it may be grounded. This means that metals or conductive-primed materials must be used. There is still a heat-resistence requirement for the object to be coated since powders require a temperature over 300°F to cure. This limits the use of powder coatings on paper, fabric, and many types of plastics.

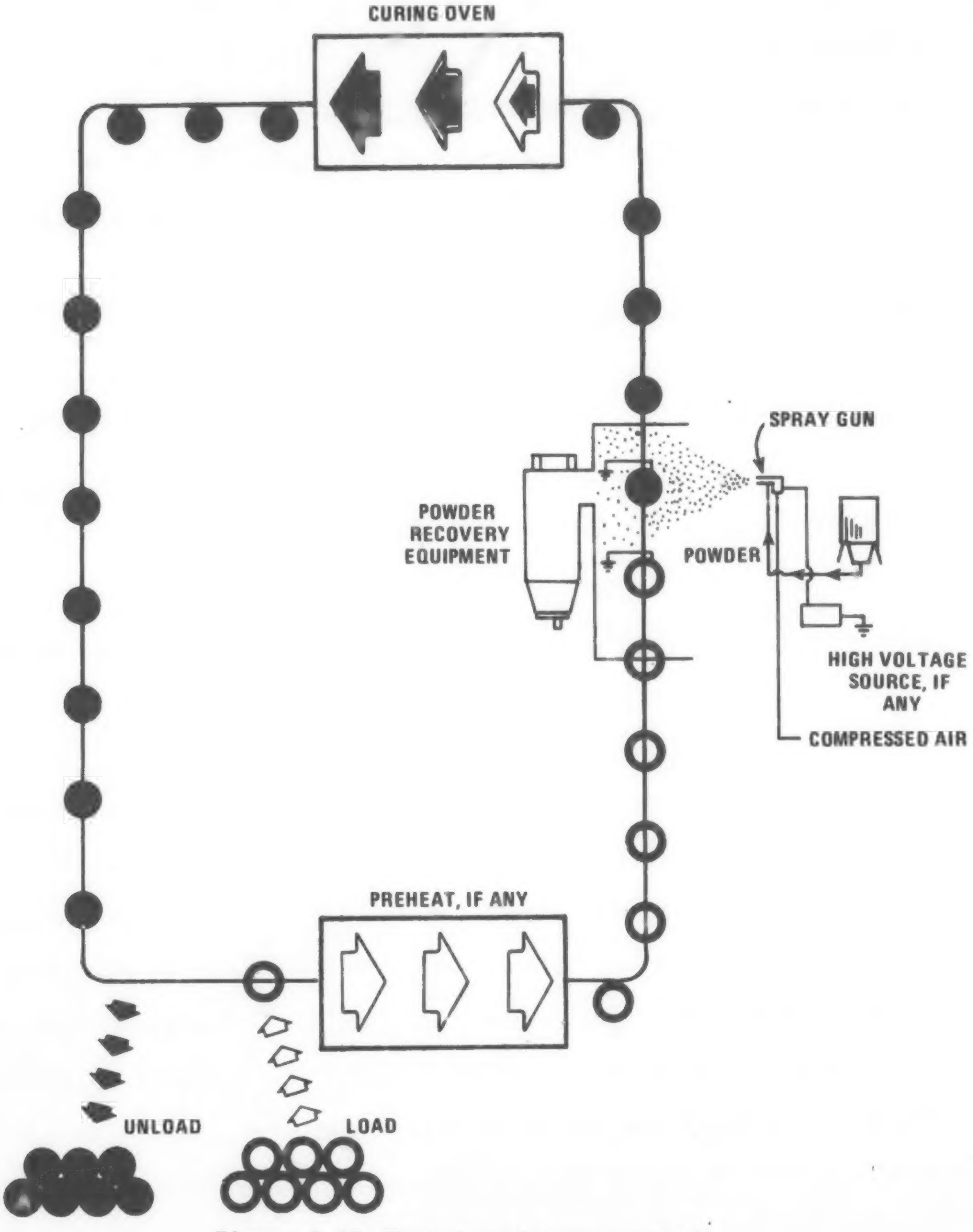
CURING OVEN
SPRAY GUN
POWDER RECOVERY EQUIPMENT
POWDER
HIGH VOLTAGE SOURCE, IF ANY
COMPRESSED AIR
PREHEAT, IF ANY
UNLOAD
LOAD

Figure 3-18. Typical powder spray operation.

(Courtesy Society of Manufacturing Engineers)

Coverage of recessed areas is better with electrostatic spray than with fluidized beds since the powder will seek out areas with less coating. Preferential coating of one side of flat objects can also be achieved, but some overlap is difficult to avoid. Masking is difficult as the powder can diffuse easily through small cracks or overlap in the masking. Finally, some shapes are difficult to coat because of "Faraday Cage" effect. This is a phenomenon that prevents charged particles from entering certain recessed areas because of repulsion from charged particles near the area.

Electrostatic spray coatings have been used for a wide variety of products including: metal chairs[14], stadium seats[15], air filters[16], telephones[17], lawn sprinklers[18], appliances[19], magnetic wire insulation[20], and building panels. General Motors and Ford have experimented with electrostatic powder spray for automobile bodies.

Conventional Fluidized Bed -- If a fluid (such as air) is passed up through a bed of granular solids with sufficient velocity, the solids will be lifted by the fluid. If the vessel design is such that the solids rise and fall in a confined area, the bed is said to be fluidized because it has many of properties of a fluid. The process of fluidization is shown in Figure 3-19. Fluidized bed application of powder involves the immersion of a heated object in the fluidized bed. Powder adheres to the surface and may be reheated to create a smoother coating. A schematic is shown in Figure 3-20. To obtain consistent coatings, it is necessary to keep the part temperature and the bed properties constant. This is done by careful control of curing time and temperature and by frequent addition of materials to the fluidized bed.

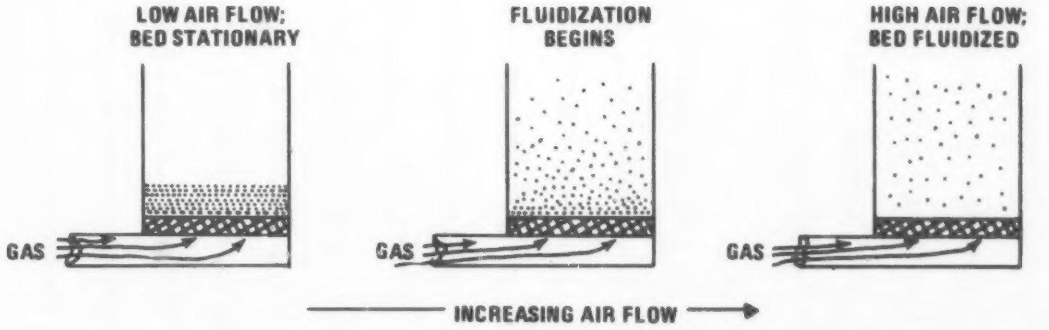
LOW AIR FLOW; BED STATIONARY
FLUIDIZATION BEGINS
HIGH AIR FLOW; BED FLUIDIZED
GAS
GAS
GAS
INCREASING AIR FLOW

Figure 3-19. Steps in bed fluidization.

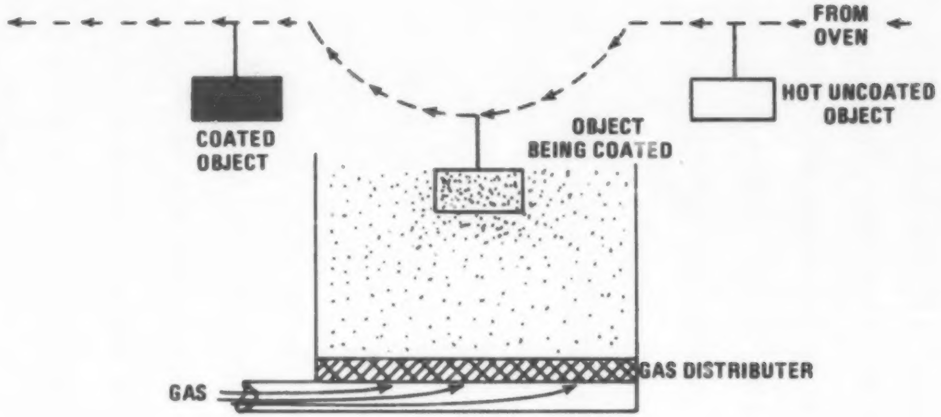
FROM OVEN
HOT UNCOATED OBJECT
OBJECT BEING COATED
COATED OBJECT
GAS DISTRIBUTER
GAS

Figure 3-20. Fluidized bed coating process.

The fluidized bed process can achieve a good quality coating of 7 to 30 mils thickness with greater consistence than dusting.[13] The objects to be coated must be capable of being heated to the necessary temperature and must have sufficient heat capacity to melt the coating. This essentially limits the method to metal products. Fluidized bed coatings do not depend on gravity alone as does dusting, but there are still difficulties with coating recessed areas or complex shapes. Fluidized beds have been successfully used in applications such as dishwasher racks and wire coating.

Electrostatic Fluidized Bed -- A relatively new electrostatic application method is electrostatic fluidized bed. The fluidized bed is a source of charged powder for application. Electrodes are placed within the fluidized bed to give the particles a charge. The charged particles repel each other and rise in the bed. As a grounded object is passed over or through the bed, the charged particles are attracted to it.[12] An oven is then used to melt the powder to a continuous coating. Figure 3-21 shows a typical line. Again, parts may be preheated to give thicker coatings.

Some powders, including polyvinyl chloride and nylons, have electrical properties that make them unusable in this process.[12] Some of the materials that can be used are: epoxies, cellulose acetate butyrates, polyesters, polypropylenes, polyethylenes, acrylics, fluorocarbons, and chlorinated polyethers.

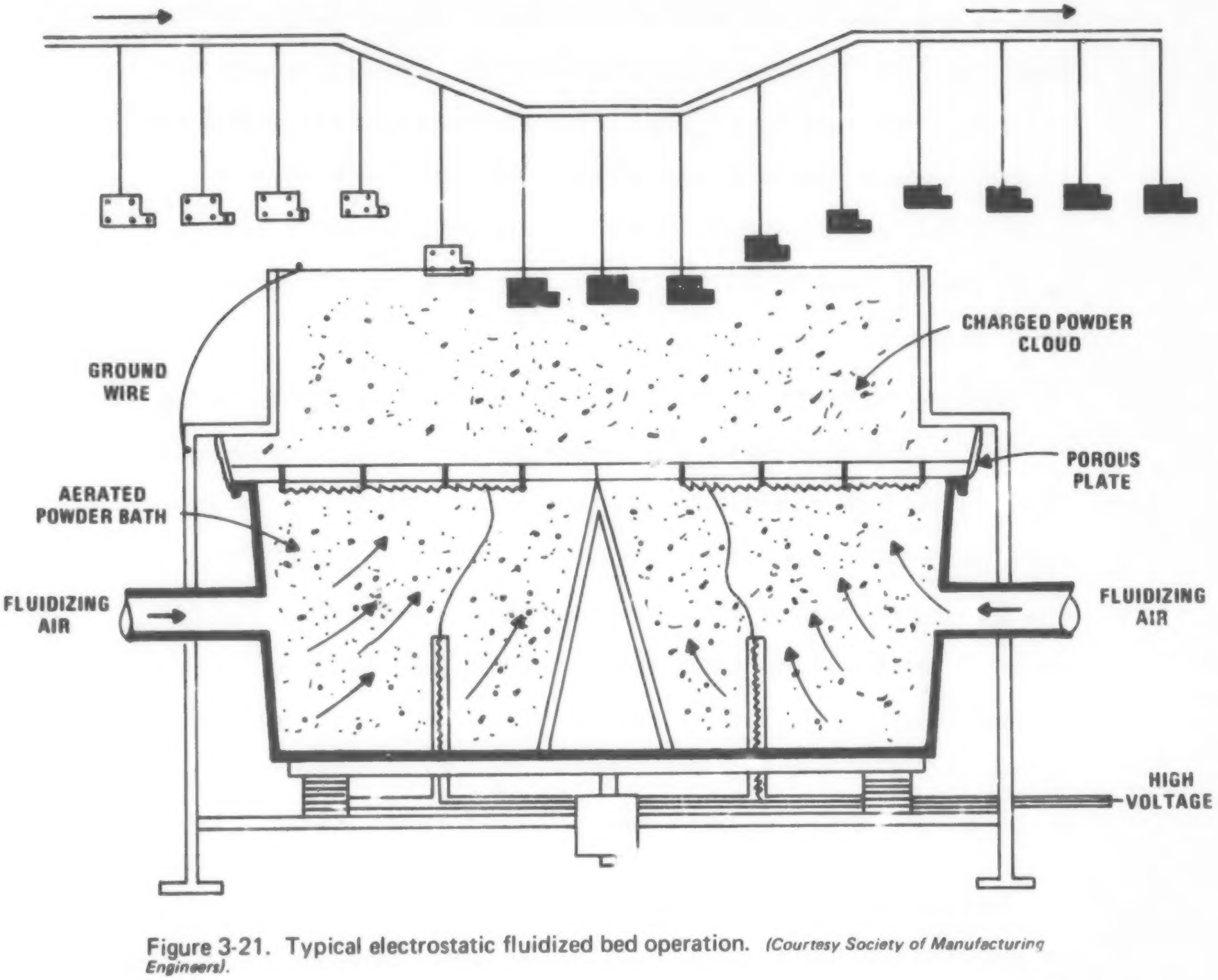
CHARGED POWDER CLOUD
GROUND WIRE
POROUS PLATE
AERATED POWDER BATH
FLUIDIZING AIR
FLUIDIZING AIR
HIGH VOLTAGE

Figure 3-21. Typical electrostatic fluidized bed operation. *(Courtesy Society of Manufacturing Engineers).*

Other electrostatic application methods that have had limited application are the electrostatic curtain and electrostatic disc methods. The electrostatic curtain method uses a traveling belt filter to hold the powder before spraying. A jet of air propels the powder through a charging area towards the object. This method is most applicable for large flat objects because it applies an equal quantity of powder to all areas of the passing surface.[13] The electrostatic disc method uses a rotating nonconductive disc as a powder distributer. The disc is coated with a resistive material that is charged and imparts a charge to the powder. This method has been used to apply powder to steel door jam sections.[13]

Dusting -- Dusting or flocking as it is sometimes called, is the earliest and simplest powder application method. It involves the application of powdered material "onto a surface which is at a temperature above the melting point of the powder so as to have the powder fuse upon hitting the surface and form a coating over the surface.[12] When powder is applied to an object at 350 to 500°F, some of it will adhere and become tacky. The material may be reheated to cause the powder to flow into a smoother coating. Application may be by automatic or manual means. Spray guns are normally used to distribute the coating.

Dusting has been used to apply powder to raw rubber goods, to prevent offset in the printing industry, to color-code steel billets, and to coat sheet plastic in original processing.[12] Dusting is limited in the consistency of coatings that can be applied.[13] Application is solely by gravity settling, so coating of complex shapes is difficult if not impossible.

3.3.4 Hot Melt Formulations -- Hot melt coatings are applied in a molten state. The molten resin film cools soon after being applied to the substrate. Because there is no solvent to evaporate, virtually 100 percent of the materials that are deposited remain as a solid part of the coating. Hot melt coatings are most often applied to paper, paperboard, cloth, and plastic.

When the hot melt coating has been applied and cooled, the film does not need further heat curing. Since the only heat required is that to melt the coating initially and to heat the coating applicator, a considerable energy savings can result compared to oven curing. Also, because an oven is not needed, less floor space is needed for the coating line. The line can be run faster with hot melts than with organic solvent-borne coatings. A chilled roll can be used to speed cooling, if necessary.

Hot melt coatings are applied at a variety of temperatures. Low melting point coatings are applied at temperatures as low as 150 to 210°F. These are materials such as waxes or paraffin coatings that are soft and easy to scratch. To improve scratch resistance, higher melting resins are added. These are usually synthetic organic compounds. Hot melt blends with melting points in the range of 300 to 450°F usually contain no paraffin, waxes, or other low melting point ingredients but rather are composed of film forming resins and plasticizers. The resultant films from such high melting point formulations show properties that are comparable to high grade solvent-borne coatings.[21]

Hot melt coatings must, of course, be applied at temperatures that are higher than the melting point of the coating. Because the substrate may be harmed by high temperatures, hot melt coatings with melting points above 400°F cannot be used for some applications. However, some extrusion coatings are heated to 600°F to achieve proper adhesion between the polymer and substrate.[22]

Hot melts may be applied in a variety of ways. Usually special heated coating equipment is required. Lower melting hot melts may be applied by heated rotogravure or roll coaters. Extrusion coaters are widely used also, especially with higher melting point materials.

Extrusion coatings are a large subclass of hot melt coatings. In this type of coating a screw extruder discharges a molten plastic sheet onto the substrate. Food containers such as milk carbons are often coated with extrusion coatings because the plastic film provdies a good moisture barrier.

Ethylene/vinyl acetate copolymer, low and medium density polyethylenes are the resins most widely used for hot melt coatings. Polyethylene forms a strong film, mixes well with other resins and waxes, has good water resistance, has good flexibility at low temperatures, and is relatively low in cost. Other resins used include vinyls, cellulose esters, alkyl esters, maleic esters, and polystyrenes. All of these materials must have viscosities suitable for application and they must be chemically stable for long periods in the molten state.

Hot melts are applicable to the paper and fabric coating industry, although only for certain applications. Thus, hot melt coatings cannot be judged to be universally applicable in the paper and fabric coating industry at this time.

3.3.5 Electrostatic Spray Coating -- Electrostatic spray coating utilizes the attractive force between materials of opposite electrical charge as an aid in applying a uniform coating to various surfaces. The method reduces overspray and waste and thereby increases the coatings application efficiency over conventional spray coating processes. In the case of solvent- and water-borne coatings, this will in effect reduce the amount of coating solids and corresponding solvent carrier needed for a specific coating job. Electrostatic spray coating can be used to apply solvent-borne, water-borne, or powder coatings. Powder coatings are discussed in Section 3.3.3.

In typical electrostatic spray coating processes where relatively nonconductive solvent-based coatings are used, coating particles are charged up to 100,000 volts with an electrode.[23] The grounded object then attracts the negatively charged particles, which are captured to form a film. In instances where conductive coatings are used, water-borne coatings, for example, it is possible to use reverse polarity, that is, charging the object to be coated and grounding the spray equipment.[24]

Electrostatic spray coating is primarily applicable to metal surface coating. It is of particular value for complex shapes. Glass, plastics, paper and fabric have been successfully coated with this technique. Corners or extreme concave shapes on objects may escape coating due to the "Faraday cage" effect.[24] This phenomenon results from the repulsive electrical forces in corners or concave areas.

Electrostatic spray coating has the potential or reducing organic emissions since it can improve the efficiency of application of solids over ordinary spray. This results in less organic solvent emissions.

3.3.6 Electron Beam Curing

3.3.6.1 Introduction -- The electron beam curing process uses high energy electrons to promote curing of electron beam-curable coatings. Electrons bombard a coating to produce free radicals throughout the coating. This initiates a crosslinking reaction that continues until the coating is cured. The entire process takes only a few milliseconds to complete.[25] Since most free radicals are terminated by oxygen. An inert atmosphere is desirable so that the surface of the coating will not be less highly crosslinked than the interior.

3.3.6.2 Energy Consumption -- The energy source for electron beam curing is electrical. The electron beam curing unit contains an electron accelerator that activates the electrons to the necessary energy state. The high energy electrons are emitted, curing the coating by a stationary or moving beam.

The energy requirements for electron beam curing are dependent on the size of the unit and the coating thickness but are typically lower than for thermal curing. There is an additional energy savings because of the instant startup and shutdown capability of the electron beam unit.

3.3.6.3 Safety -- Electron beam curing units must be shielded properly to avoid radiation exposure. According to occupational Safety and Health Administration regulations, exposure should not exceed 5 millirems of radiation in 1 hour and 100 millirems in any 5 consecutive days.[26]

Some electron beam-curable coatings may contain monomers that are toxic. Caution should be taken when using such monomers.

3.3.6.4 Organic Solvent Emissions Reduction Potential -- There have been few, if any, tests performed to quantify organic vapors emitted during the curing process. It is generally assumed that some low molecular weight organic compounds are emitted during curing even though all the components are reactive. There also may be some ozone generated from the curing process itself.[27]

3.3.6.5 Application to Industries Studied -- The use of electron beam curing is most effective on flat surfaces where the electron beam strikes the surface vertically. If the beam strikes the surface at an angle closer to the horizontal, the amount of absorbed energy can be too small and the coating will not cure properly.

Electron beam curing, unlike ultraviolet light curing, can cure thick and pigmented coatings because of the penetrating power of the electrons.

Because electron beam curing uses relatively new technology, the coatings necessary for the electron beam curing process are in the early stages of research and development. The use of electron beam curing is very limited at the present time.

3.3.7 Ultraviolet Curing

3.3.7.1 Introduction -- In ultraviolet curing, ultraviolet light reacts with photosensitizers in the coating to initiate crosslinking to form a solid film. The basic components of an ultraviolet curable coating are: an ultraviolet-curable base polymer, diluent monomers, and ultraviolet photochemical initiators.[28]

The ultraviolet-curable polymers provide most of the desired coating properties. The diluent monomers decrease the viscosity of the polymers, increase the crosslinking density, and improve other features of the coating such as gloss, hardness, and curing speed. The photochemical initiators are unstable chemicals that form free radicals when bombarded by ultraviolet light to initiate the crosslinking process.[29]

The energy source used for ultraviolet curing is electrically produced ultraviolet light energy such as from mercury vapor lamps. The use of ultraviolet light for curing is most effective on flat surfaces where the light reaches the surface vertically. When the ultraviolet light strikes a surface at an angle closer to the horizontal, the amount of absorbed light can be too small for effective curing. Obviously, no curing will occur if an area is shielded from the light.

3.3.7.2 Performance and Appearance -- The actual performance and appearance of ultraviolet-curable coatings is not only dependent on the base polymers, diluent monomers, and photochemical initiators, but also on other agents such as pigments, fillers, and mar resistors added to the coating to provide the desired properties.

In certain industries, the use of ultraviolet light curing has been successful, although this success has been limited mostly to semitransparent coatings, such as inks. Ultraviolet cured polyester based coatings have made a significant penetration into the forest products industry as filler coatings for practiceboard. Most uses of ultraviolet coatings, however, are still in the research and development stage. Major problems are curing of thick coatings and coatings with pigmentation. The main difficulty with pigmentation is that the pigment particles absorb or reflect ultraviolet light, thus reducing the light energy available to cure the coatings in the deeper layers of the coating.

3.3.7.3 Energy Consumption -- Because little if any flammable solvent is emitted, the amount of dilution air flow through ovens can be greatly reduced. There is a substantial decrease in energy usage compared with thermal curing. An ultraviolet curing unit may use only one-third the energy of a standard thermal oven.[30]

3.3.7.4 Safety -- The ultraviolet curing equipment must be shielded properly to avoid exposure of the equipment operator. Exposure at short distances can cause severe burns to the skin and the eyes.[31]

Certain ultraviolet coating materials may produce skin and eye irritation. Others, such as those containing "the more volatile crylic monomers, are considered toxic and hazardous chemicals."[31] The handling of ultraviolet-curable coatings requires care and caution.

3.3.7.5 Organic Solvent Emissions Reduction Potential -- There have been few, if any, emission tests performed to determine whether volatile organics are emitted during ultraviolet curing. Some low molecular weight organic compounds are probably emitted during the ultraviolet curing process even though all the components of the coating are reactive.

3.4 REFERENCES

1. Package Sorption Systems Study, MSA Corporation, Evans City, Pa., Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C. under Contract EHSD 71-2. Publication No. EPA R2-73-202. April 1973.
2. Rolke, R.W. et al. Afterburner Systems Study, Shell Development Company, Emeryville, Cal., Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C. under Contract No. ESHD 71-3. Publication No. EPA-R2-72-062. August 1972.
3. Control Technology for Hydrocarbons and Organic Solvent Emissions from Stationary Sources, U.S. Department of Health, Education and Welfare, National Air Pollution Control Administration, Washington, D.C. Publication No. AP-68, March 1970.
4. Wildman, G.C., and B.G. Bufkin. Waterborne's Position in the Spectrum of Industrial Coatings: Comparison to Solvent Types and Availability. American Paint and Coatings Jounral, p. 18-22 and 56-59. July 14, 1975.
5. Anisfield, J. Powder's Competition. Canadian Paint and Finishing. December 1974.
6. "Electroless Electrocoat" now in Production at Chrysler. Industrial Finishing 51(10):72, October, 1975.
7. Schrantz, Joe. How Autodeposited Coating Benefits Chrysler. Industrial Finishing (51(11):14-22. November 1975.
8. Kachman, N.C. General Motors Corporation, Warren, MI. Letter to G.M. Hansler, Region II, Environmental Protection Agency, New York, N.Y. February 11, 1974.

9. Conversation of J.A. McCarthy, U.S. Environmental Protection Agency with Chrysler Corporation, Detroit, MI. November 12, 1975.

10. Boston Transportation Control Plan, Federal Register, p. 25166. June 1975.

11. Coil Coaters Discuss Anti-Pollution Systems. Industrial Finishing. 49(7): 48-54. July 1973.

12. Miller, E.P. and D.D. Taft. Fundamentals of Powder Coating. Society of Manufacturing Engineers. Dearborn, MI. 1974.

13. Powder Coating: The Problems and the Promises. Products Finishing. 36(8), May 1972.

14. High-productivity EPS System at Bunting. Industrial Finishing. 48(3), March 1972.

15. Robinson, G.T. Painting Stadium Seats. Products Finishing. 40(4): 50-54. January 1976.

16. Vinyl-Coated Wire Screens Resist Salt in Air Filters Aboard Ship. Powder Coating World. II(2): 26, 2nd Quarter 1975.

17. Powder Coating Is a New Answer at GTE Electric. Powder Finishing World II(2): 30, 2nd Quarter 1975.

18. Powder System Highly Satisfactory at Rain Bird. Powder Finishing World II(2): 33-34, 2nd Quarter 1975.

19. High-Production Thin Film Powder Coating a Success at Rival. Products Finishing. 39(5): 32-87, February 1975.

20. Powder Coating Used as Insulation for Magnet Wire. Products Finishing. 39(5): 94-95, February 1975.

21. Miller, B.C. and P.H. Yoder. Hot Melt Coatings. In: Industrial

and Specialty Papers, Volume I - Technology. Mosher, R.H. and D. Davis (eds.). New York, Chemical Publsihing Col, 1968.

22. Reichner, R.F. Extrusion Coating. In: 1973-1974 Modern Plastics Encyclopedia, New York, McGraw-Hill, Inc., 1974. P. 315-320.

23. Roberts, A.G. Organic Coatings, Properties, Selection and Uses, U.S. Department of Commerce, National Bureau of Standards, Washington, D.C. February 1968.

24. Electrostatic Spraying of Water-Borne Paints. Poll, G.H., Jr. (ed.) Products Finishing 40(4): 34-41, January 1976, p. 34-41.

25. Berbeco, G.R. and S.V. Nablo. Electron Beam Curing. Paint and Varnish Production. 64(9): 39-42, August 1974.

26. Hoffman, C.R. Electron Beam Curing a Non-Polluting System, High Voltage Engineering Corporation, Burlington, Mass.

27. Miranda, T.J. and T.F. Huemmer. Radiation Curing of Coatings. Journal of Paint Technology. 41(529): 118-128, February 1969.

28. Rybny, C.B.,et al. Ultraviolet Radiation Cured Coating. Journal of Paint Technology. 46(596): 60-69, September 1976.

29. Billmeyer, F.W., Jr. Textbook of Polymer Science. Interscience Publishers of John Wiley and Sons, New York, N.Y. March 1966.

30. Radiation Curing Goes Begging for Coaters. Iron Age. p. 43-52, August 18, 1975.

31. Shahidi, J.K. et al. Multifunctional Monomers for UV Cure. Paint and Varnish Production. August, 1974.

4.0 COST OF VOLATILE ORGANIC CONTROL

4.1 Summary

This chapter shows that many factors can affect the investment and annual cost of hydrocarbon control (Section 4.2.1); thus a wide range in control costs at existing facilities is anticipated. Cost estimates made for incineration and adsorption (4.2.2) indicate that for low hydrocarbon concentrations (around 100 ppm), carbon adsorption is the more economical of the two control alternatives. For control of high hydrocarbon concentrations (around 25 percent of the LEL), carbon adsorption is more economical and can even make money if recovered solvents can be credited at market value; if no value is given for recovered solvents, then incineration with primary heat recovery is more economical than adsorption at high LEL concentrations.

With regard to cost effectiveness, (cost per ton of volatile organic removed), it is found that control of high concentrations is more economical than is control of low concentrations by roughly one order of magnitude (4.2.3). It is beyond the scope of this chapter to evaluate the affordability of various volatile organic control costs for the industries affected, because each industry has a unique financial position.

4.2 General Discussion of Costs

For most business ventures, an adequate return on investment is the most important requirement to be evaluated before investment. Air pollution control often does not provide any return on captial investment--the objective is to comply with a given emission standard. The primary criteria for selection is ability to achieve the required emission reduction. If several methods exist to control emissions, the problem then becomes one of evaluating the cost of feasible alternatives to determine the preferred alternative.

To evaluate the cost of feasible alternatives, it is important to understand the factors that affect costs and the magnitude of these costs. Factors affecting the investment and annual cost of control are given in Section 4.2.1. Costs of hydrocarbon control for two types of control technology is given in Section 4.2.3. The discussion is aimed primarily at add-on control equipment. It is beyond the scope of this discussion to consider the cost of process and material changes to achieve compliance with hydrocarbon regulations at existing facilities due to the almost unlimited variety in processes and facilities.

4.2.1 Factors Affecting Investment and Annual Cost

4.2.1.1 Process Characteristics -- Before one can estimate investment and annual cost of control, one must first know certain characteristics (gas stream volume and temperature, for example) of the source of pollution because these characteristics affect selection and sizing of the control equipment. In some cases only one control alternative may be feasible; however, in most cases two or more alternatives are feasible. A good knowledge of the specific source of pollution is advisable because process or input material changes may be the least expensive method of controlling volatile organic emissions.

4.2.1.2 Present Degree of Control -- Another important factor to consider is the present degree of control of volatile organics versus the required degree of control. Industries may have control equipment but must achieve more reduction in emissions to comply with a standard. Upgrading or modifying the existing equipment is usually the least expensive in these cases but complete replacement of the existing control equipment with more efficient equipment is another alternative. Application of engineering ingenuity is often needed to solve problems related to volatile organic control at existing facilities.

If process modification or upgrading existing control equipment is not possible, the use of additional add-on collection equipment must be examined. Once the types of controls capable of achieving the desired control level are chosen, one can choose the equipment with minimum total installed cost. (The cost of the control equipment itself can sometimes be a small fraction of the total system installed cost.) Tables 4-1 and 4-2 show the items typically included in the investment and annualized operating cost of add-on control systems.

4.2.1.3 Plant Facility Characteristics -- Availability of physical space for the control system, utilities to operate the control system, forms and quantity of heat recovery possible at the facility, and ability to utilize recovered products are classified as plant facility characteristics that affect selection and costs of organic vapor control technology.

4.2.2 Organic Vapor Control Costs

4.2.2.1 Incineration -- Incineration can be an economical control alternative if heat recovery techniques can be utilized. To illustrate the importance of heat recovery, three cases were investigated:

1. No heat recovery.
2. 35 percent primary heat recovery.
3. 35 percent primary heat recovery and 55 percent secondary heat recovery of the remaining 65 percent.

For each case, cost estimates[1] were made for three inlet flow rates (5,000, 15,000, and 30,000 scfm), two inlet stream temperatures (70 and 300°F), and three stream concentrations (0, 15, and 25 percent of the LEL). Other assumptions used in developing the estimates are given in Table 4-3.

Table 4-1. TYPICAL ITEMS INCLUDED IN INVESTMENT COST OF ADD-ON CONTROL SYSTEMS

° Basic Collection Equipment

° Auxiliary Equipment

·Air movement equipment

Fans and blowers
Hoods, ducts
Electrical (motors, starters, wire conduits, switches, etc.)

·Liquid movement equipment

Pumps
Electrical (motors, starters, wire conduits, switches, etc.)
Piping and valves
Settling tanks

·Instrumentation for measurement and control of:

Air and/or liquid flow
Natural gas and/or fuel oil flow
Temperature and/or pressure
Operation and capacity
Power

° Research and Development - this might include gas stream measurement, pilot plant operations, personnel costs, etc.

° Installation

Labor to install
Cleaning the site
Yard and underground
Building modification
Inspection
Support construction
Protection of existing facilities
Supervising and engineering
Startups

° Storage and Disposal Equipment

° Contingencies

° Sales Tax

Table 4-2. TYPICAL ITEMS INCLUDED IN ANNUAL COSTS OF ADD-ON CONTROL SYSTEMS

- Capital Charges
- Operating Costs
    - Utilities needed to operate the control equipment
    - Materials consumed (such as fuel) in operating the control system
    - Waste disposal operations
- Overhead
    - Property taxes
    - Insurance
- Maintenance Costs
    - Replacement of parts and equipment
    - Supervision and engineering
    - Repairs
    - Lubrication
    - Surface protection (such as cleaning and painting)
- Offsetting Cost Benefits from Operating Control System (such as recovery of valuable by-product)

Table 4-3. ASSUMPTIONS USED IN DEVELOPING COST ESTIMATES FOR CATALYTIC AND NONCATALYTIC INCINERATORS

- ° Noncatalytic incinerators designed for both oil and natural gas operation.
- ° Catalytic incinerators designed for natural gas and propane operation.
- ° Catalytic incinerators capable of 800°F operation below 6 percent LEL; 1200°F design capability for operation from 6 percent to 25 percent LEL.
- ° 3-year catalyst life.
- ° Costs based on outdoor location.
- ° Rooftop installation requiring structural steel.
- ° Fuel cost of $1.50 million Btu (gross). Correction factors are provided to determine operating costs at higher fuel prices.
- ° Electricity at $0.03 kw-hr.
- ° Depreciation and interest was taken as 16 percent of capital investment. Annual maintenance was assumed to be 5 percent of capital cost, taxes and insurance, 2 percent, and building overhead, 2 percent.
- ° Direct labor assessed at 0.5 hr/shift x 730 shifts/yr x $8.00/hr = $2920/yr direct labor expense.
- ° Operating time: 2 shifts/day x 8 hr/shift x 365 days/yr = 5840 hr/yr. Correction factors are provided to determine annual cost at different operating times.
- ° The noncatalytic incinerator utilized was based on:
    - · 1500°F capability.
    - · 0.5-second residence time.
    - · Nozzle mix burner capable of No. 2 thru No. 6 oil firing.
    - · Forced mixing of the burner products of combustion using a slotted cylinder mixing arrangement. This cylinder allows the burner flame to establish itself before radial entry of the effluent thru slots in the far end of the cylinder.
    - · A portion of the effluent to be incinerated is ducted to the burner to serve as combustion air. This allows the burner to act as a raw gas burner, thus saving fuel over conventional nozzle mix burners. This design can only be used, however, when the O_2 content of the oven exhaust is 17 percent by volume or above.

°The catalytic afterburner was costed for two design points, 800 and 1200°F. the higher temperature design is required for LEL levels exceeding 6 percent. (At 600°F into the catalyst and a 6 percent LEL, the outlet temperature of the catalyst is approximately 800°F; at a 25 percent LEL condition and a minimum initiation temperature of 500°F, the catalyst reaches an outlet temperature of around 1200°F.

Annual control cost curves are given in Figures 4-2 through 4-5, Figures 4-7 through 4-10, and Figures 4-12 through 4-15 for the three cases investigated. The costs obtained from these figures include a fuel cost of \$1.50/million Btu and operating time of 5840 hr/yr. If fuel cost and/or operating time for a specific installation differ from these values, the annual costs obtained from these figures can be adjusted by correction factors obtained from Figures 4-16 through 4-19. The annual costs read from the figures are multiplied by the correction factor(s). The cost effectiveness can be corrected by the following equation:

$$CE_c = CE_i \times F_f \times F_h \times \frac{5840}{\text{actual hours operated}}$$

where: CE_c = corrected cost effectiveness

CE_i = Cost effectiveness read from the appropriate figure

F_f = Correction factor for fuel cost

F_h = Correction factor for hours operated

The costs given in annual cost figures include depreciation and interest for the capital investment at a minimum retrofit cost situation. In cases where retrofit difficulties cause the installed cost to be increased substantially, an appropriate multiplying factor (retrofit difficulty factor) can be used to obtain the increased capital cost. The increase in annual cost, for a given retrofit difficulty factor, will be a varying amount for the different cases of vapor concentration, initial temperature, and heat recovery. The increase in the annual cost for the different cases is given in Tables 4-4 and 4-5. The annual cost is first read from the applicable figure, then is increased by the percentage given in Tables 4-4 and 4-5 under the appropriate difficulty factor.

Based upon the results of the cost estimates, cost curves were developed (Figures 4-1 through 4-15). Because of the unique plant facility characteristics, actual control costs for some plants can be substantially higher than estimates given here. For figures that give total annual cost, cost effectiveness information is also presented, that is, the cost per ton of hydrocarbon removed. Cost effectiveness information is a useful criterion when trying to devise air pollution control strategies to reduce the total amount of a pollutant emitted at a minimum cost. Cost effectiveness is discussed further in Section 4.2.3.

Installed cost of incinerators -- Figures 4-1, 4-6, and 4-11 give the installed cost for incinerators designed for (1) no heat recovery, (2) primary heat recovery, and (3) primary and secondary heat recovery. The costs were intended to represent typical retrofit situations. However, further investigation has revealed that the costs are more representative of the minimum retrofit situation, essentially the same as installation during the construction of a new plant. The installed cost in more typical retrofit situations will be 1.5 to 2 times the values shown in Figures 4-1, 4-6, and 4-11. In very difficult cases, the cost can be 3 to 5 times that shown in the figures.

The average installed cost of incinerators with primary heat recovery is roughly 25 to 30 percent greater than incinerators without heat recovery. Incinerators with primary and secondary heat recovery have roughly 50 to 60 percent higher installed costs than incinerators without heat recovery.

Annual control cost of incinerators -- The annual control costs for incinerators given in this section include the items shown in Table 4-3. (Annual depreciation is viewed in this study as a cost, not as a credit against taxable income.) Thus, the analysis is simplified, but the annual control cost may be overstated. However, given the wide range in cost of retrofitting control equipment at existing facilities, this approach is deemed acceptable.)

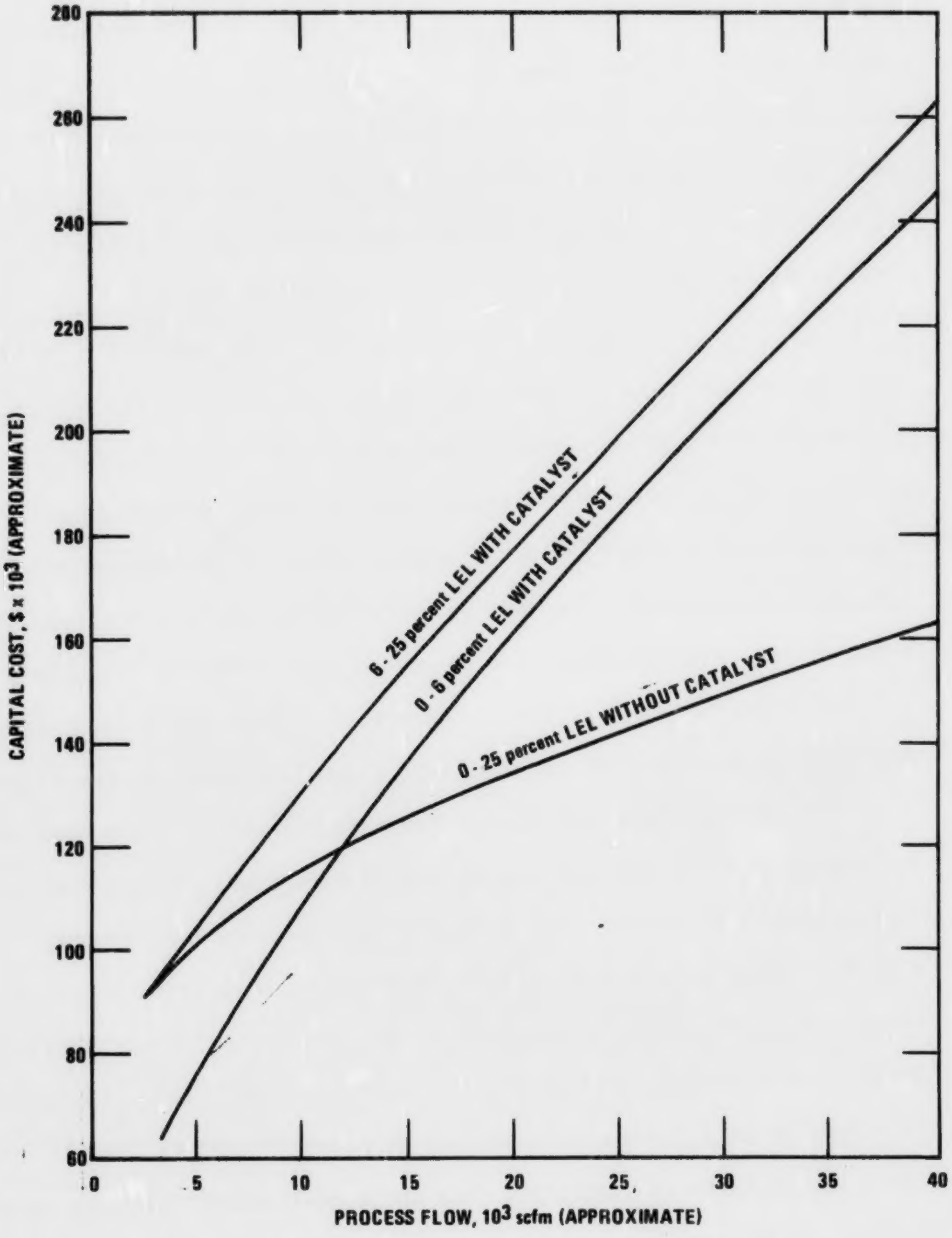

Figure 4.1. Capital cost for direct flame and catalytic afterburners without heat recovery (70 - 300 °F process gas inlet) - Case 1.

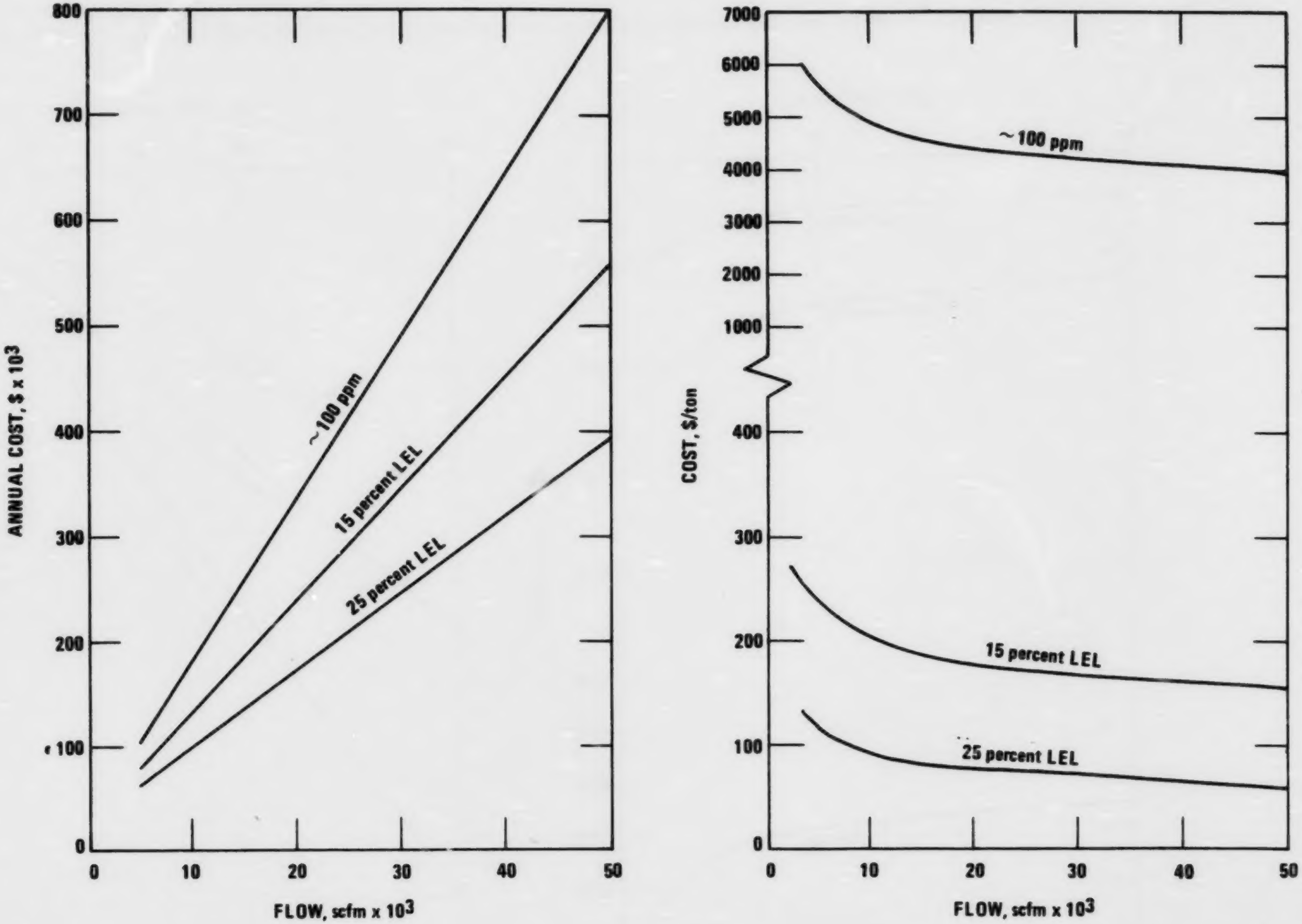

Figure 4-2. Annual cost and cost-effectiveness of direct flame incinerators. (No heat recovery - process temperature = 70 °F) - Case 1.

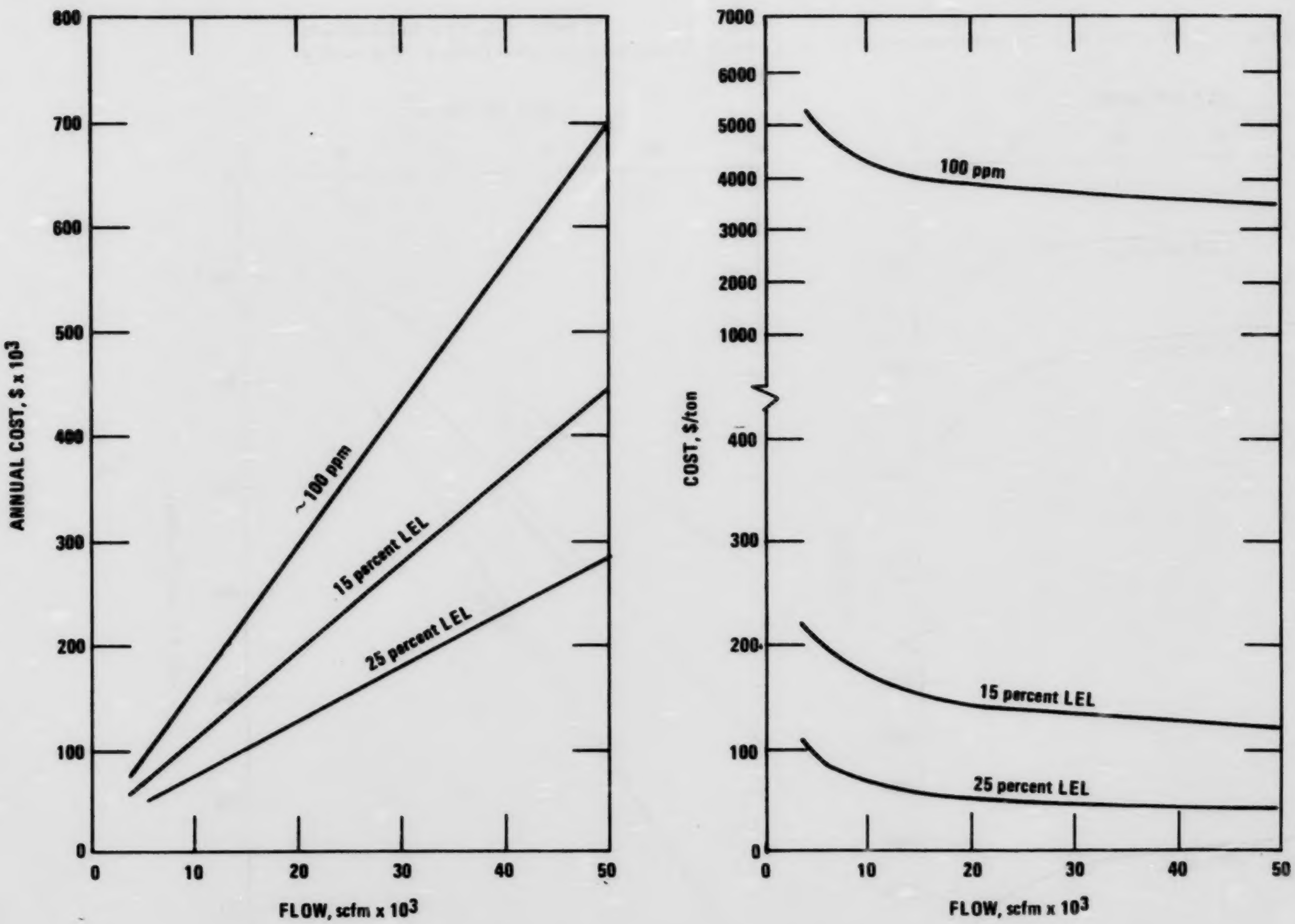

Figure 4-3. Annual cost and cost-effectiveness of direct flame incinerators (no heat recovery - process temperature = 300 °F) - Case 1.

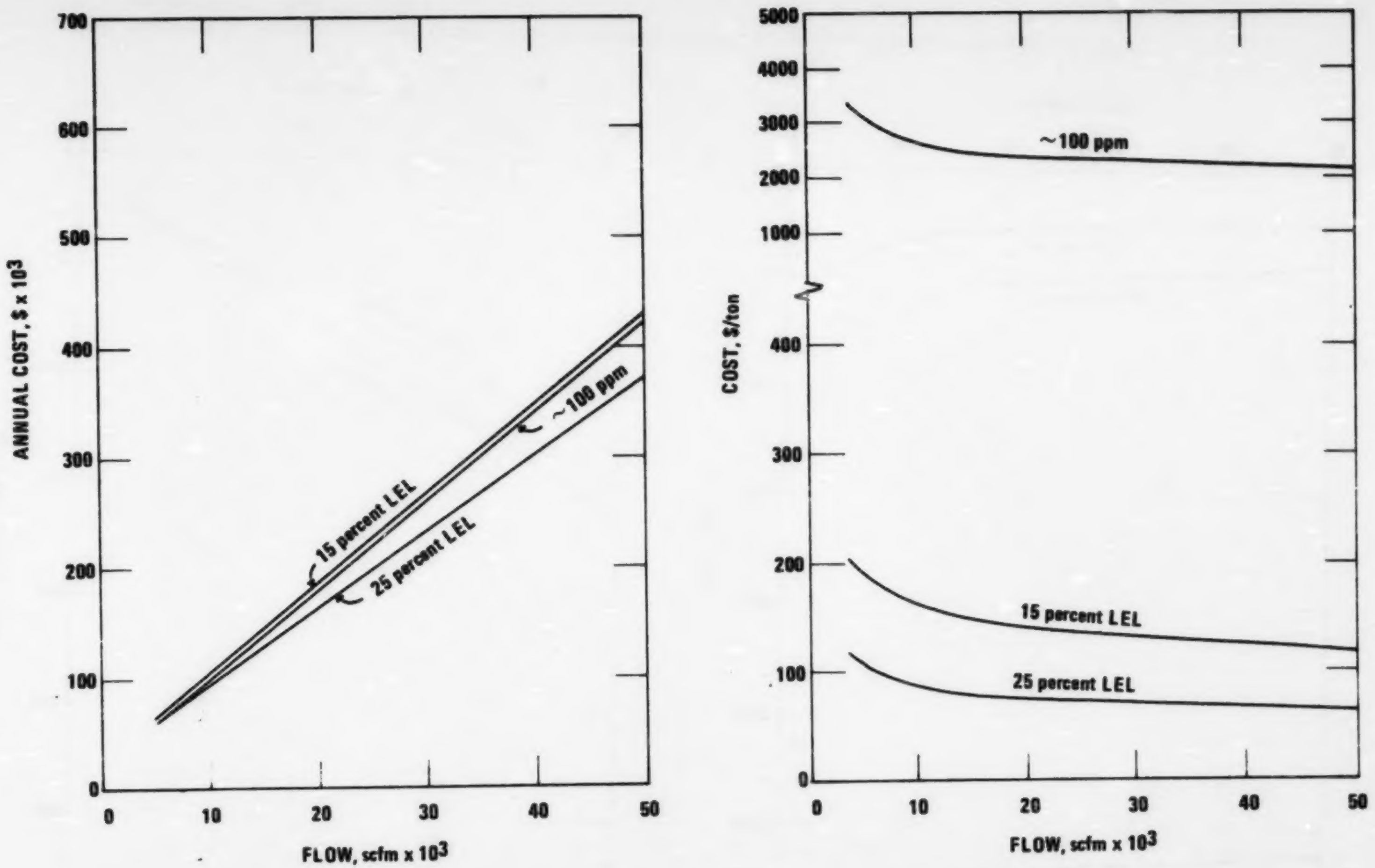

Figure 4-4. Annual cost and cost-effectiveness of catalytic incinerators (no heat recovery - process temperature = 70 °F) - Case 1.

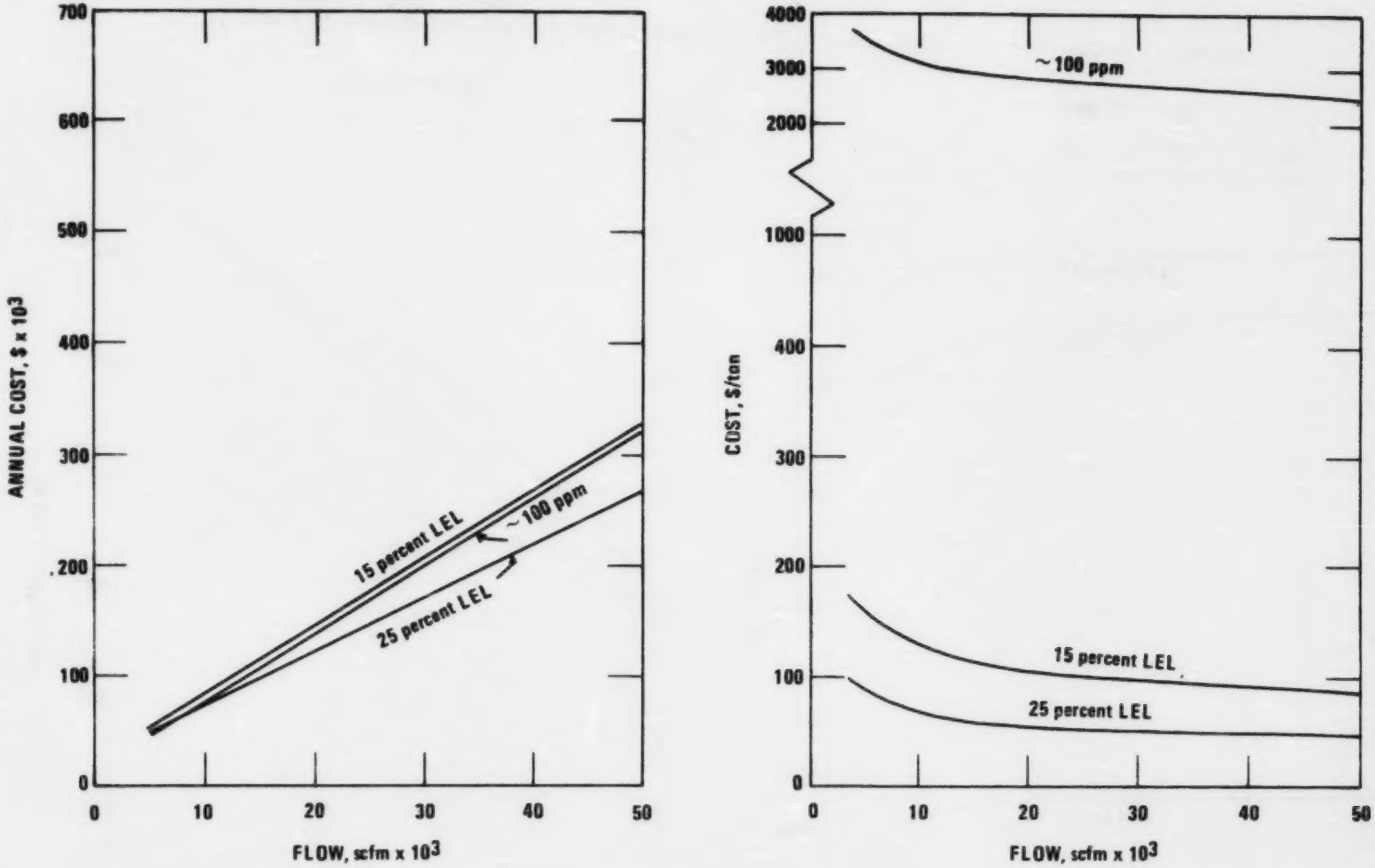

Figure 4-5. Annual cost and cost effectiveness of catalytic incinerators (no heat recovery - process temperature = 300 °F) - Case 1.

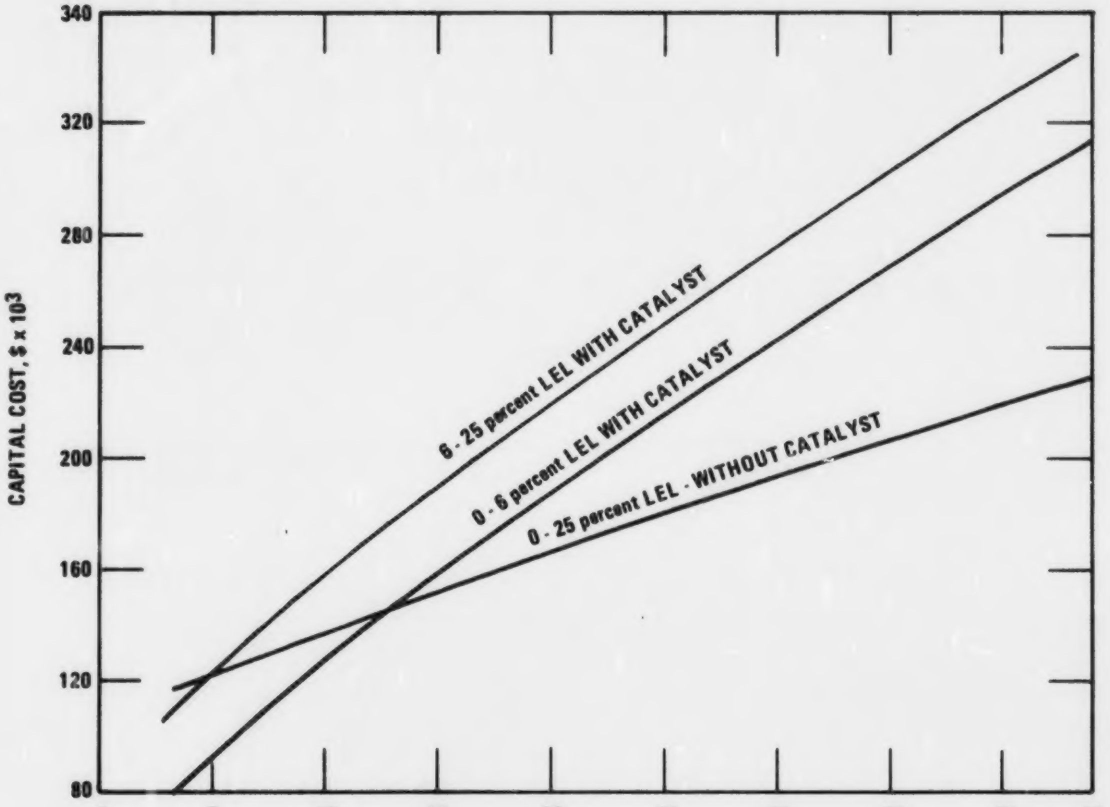

Figure 4-6. Capital cost for direct flame and catalytic afterburners with primary heat recovery (70 - 300 °F process gas inlet) - Case 2.

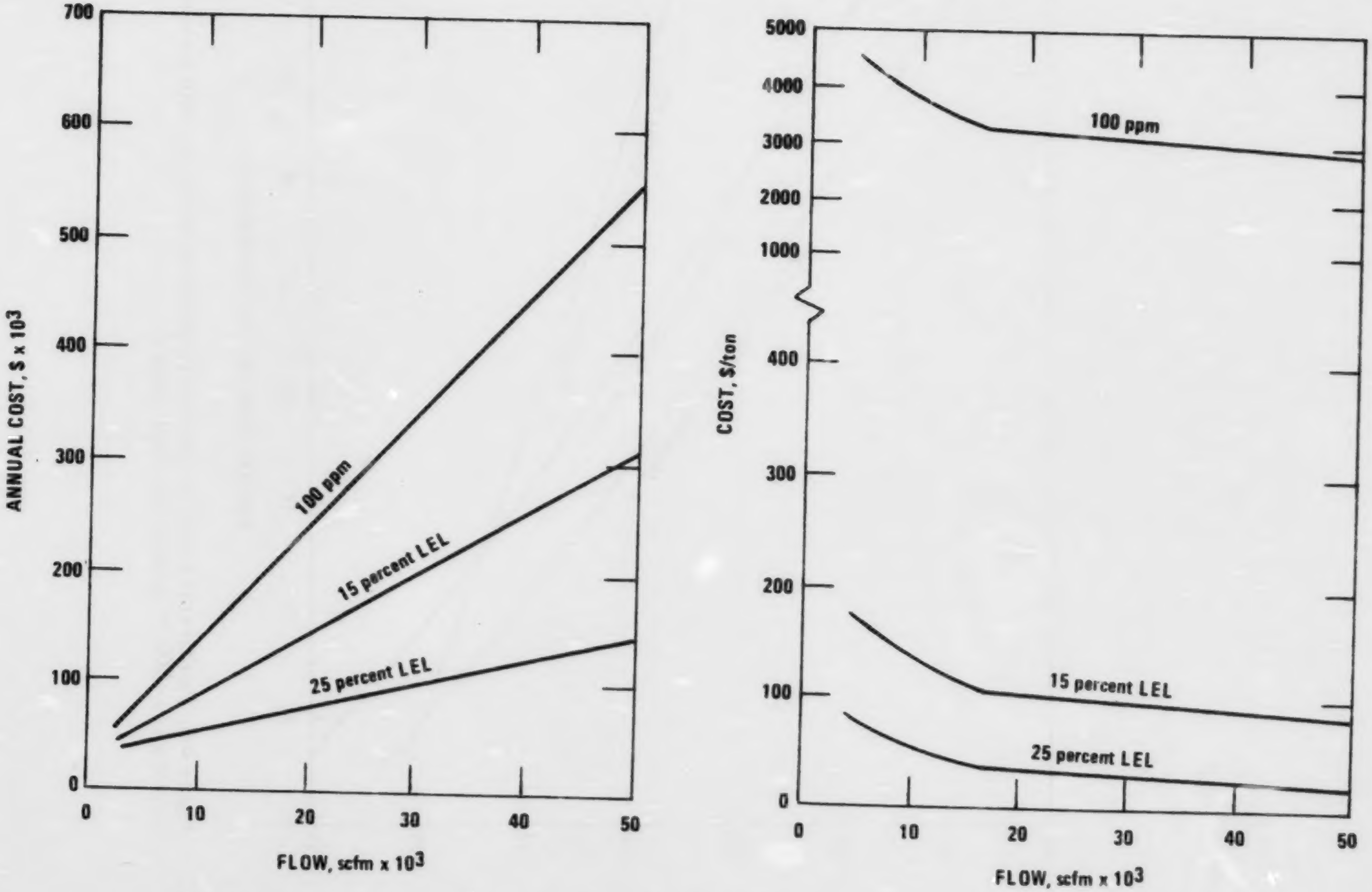

Figure 4-7. Annual cost and cost-effectiveness of direct flame incinerators (primary heat recovery - process temperature = 70 °F) - Case 2.

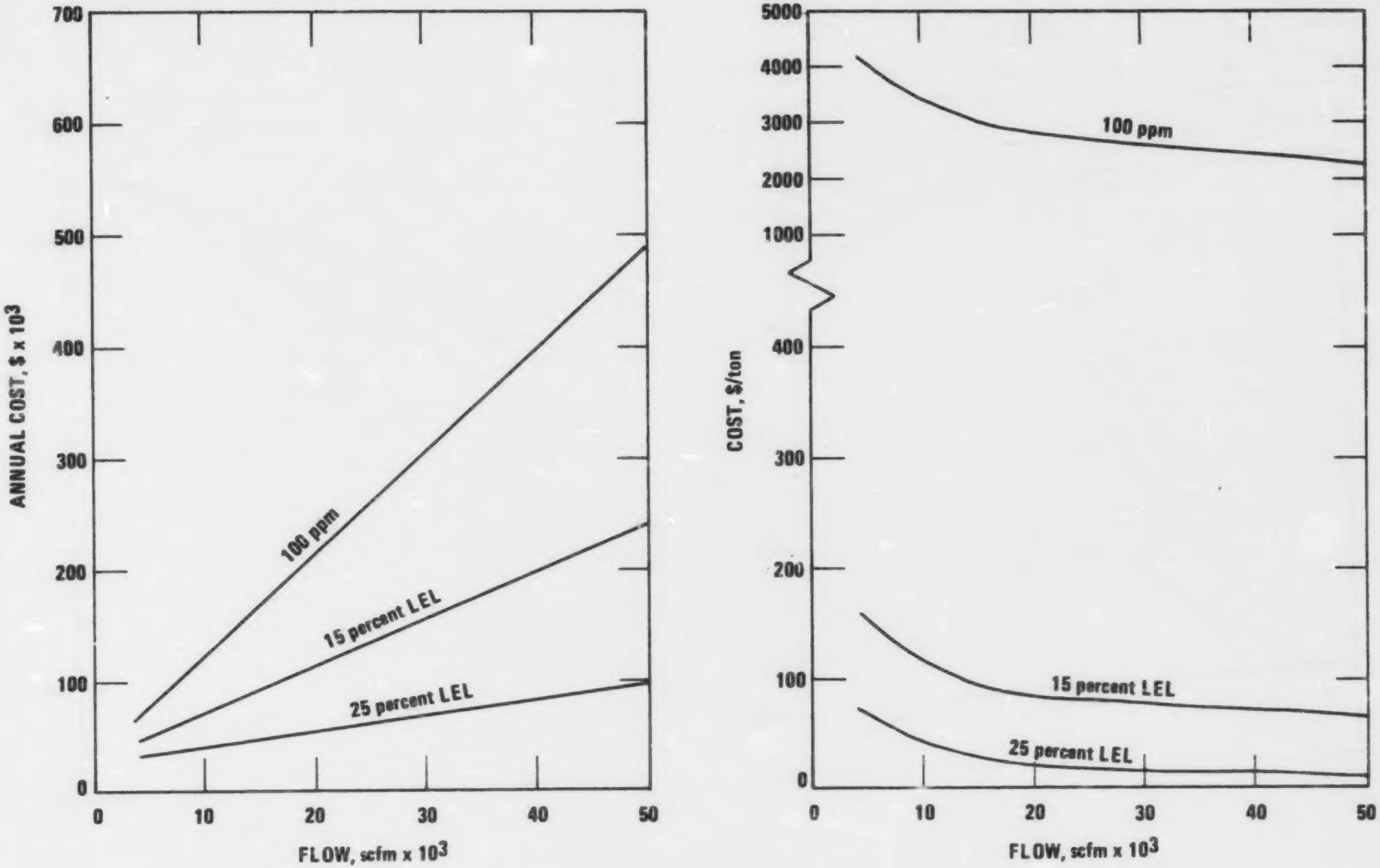

Figure 4-8. Annual cost and cost-effectiveness of direct flame incinerators (primary heat recovery - process temperature = 300 °F) - Case 2.

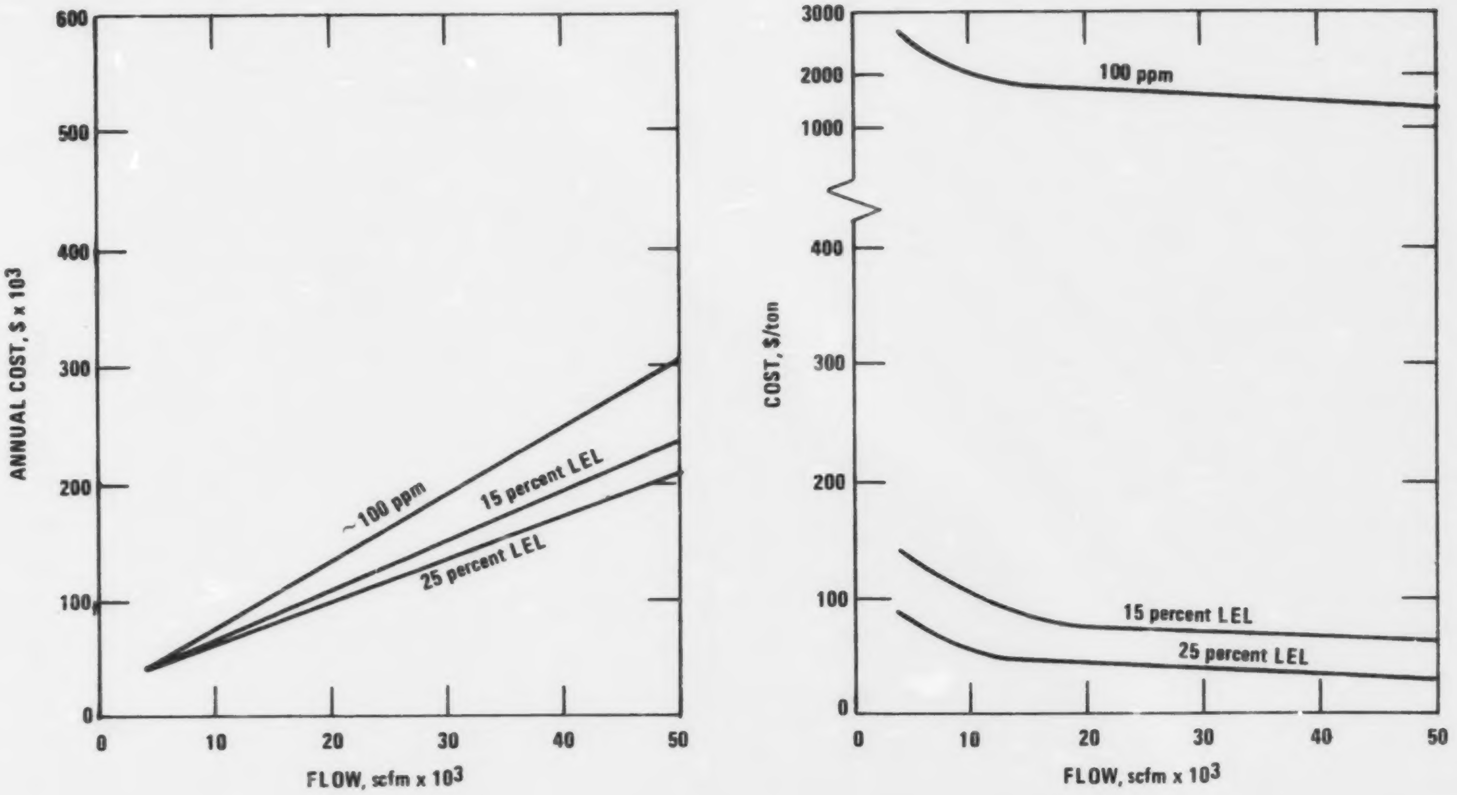

Figure 4-9. Annual cost and cost-effectiveness of catalytic incinerators (primary heat recovery - process temperature = 300 °F) - Case 2.

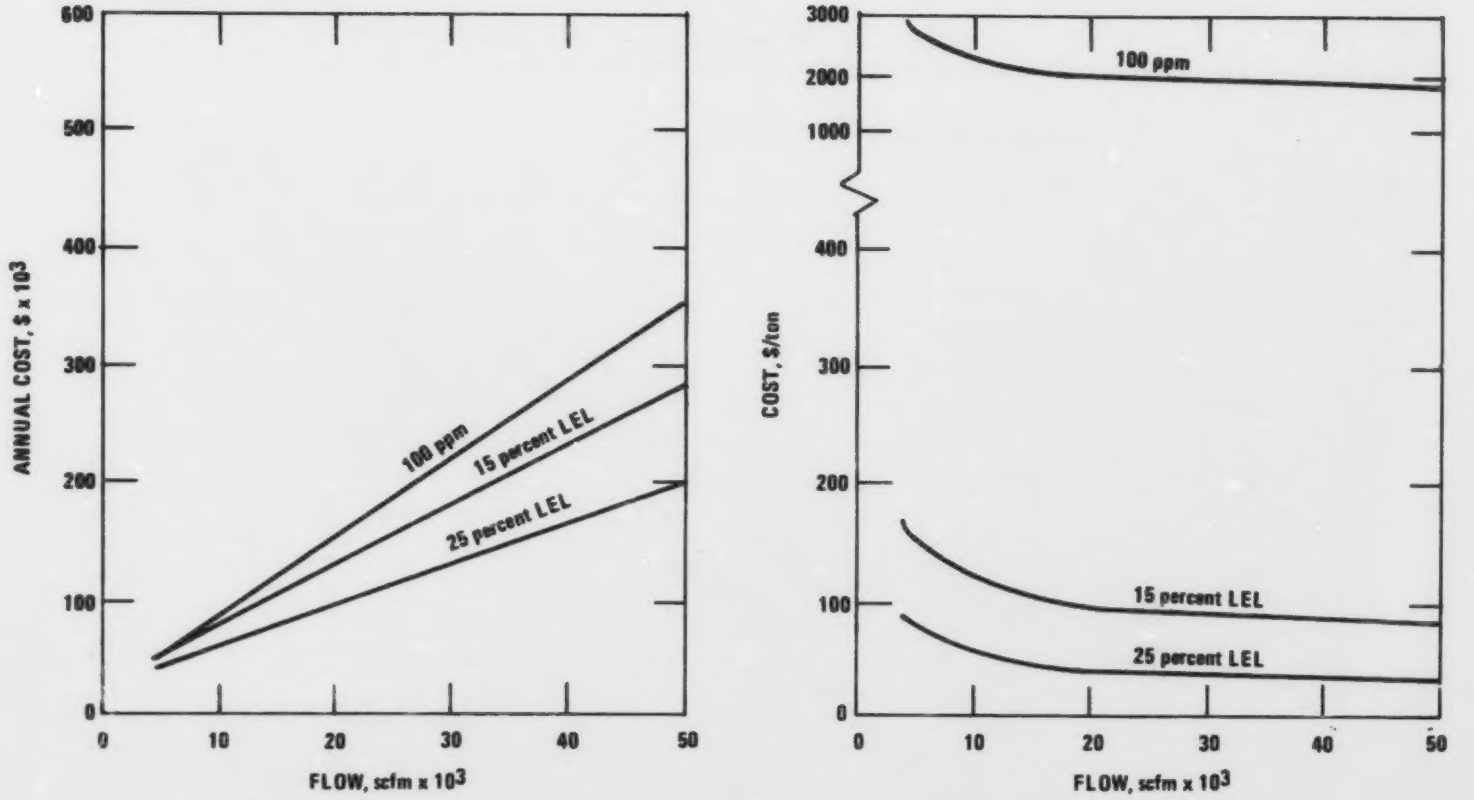

Figure 4-10. Annual cost and cost effectiveness of catalytic incinerators (primary heat recovery - process temperature = 70 °F) - Case 2.

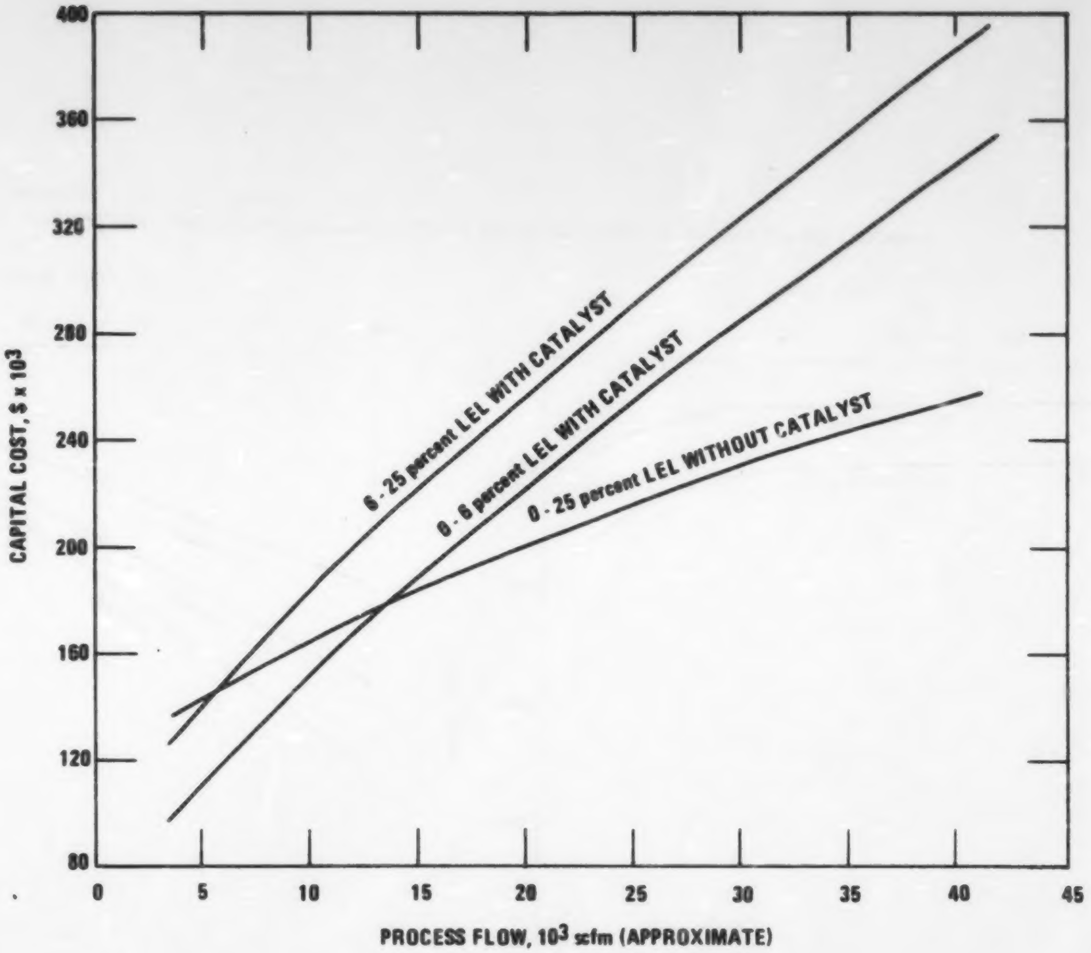

Figure 4-11. Capital cost for direct flame and catalytic afterburners with primary and secondary heat recovery (70 - 300 °F process gas inlet) - Case 3.

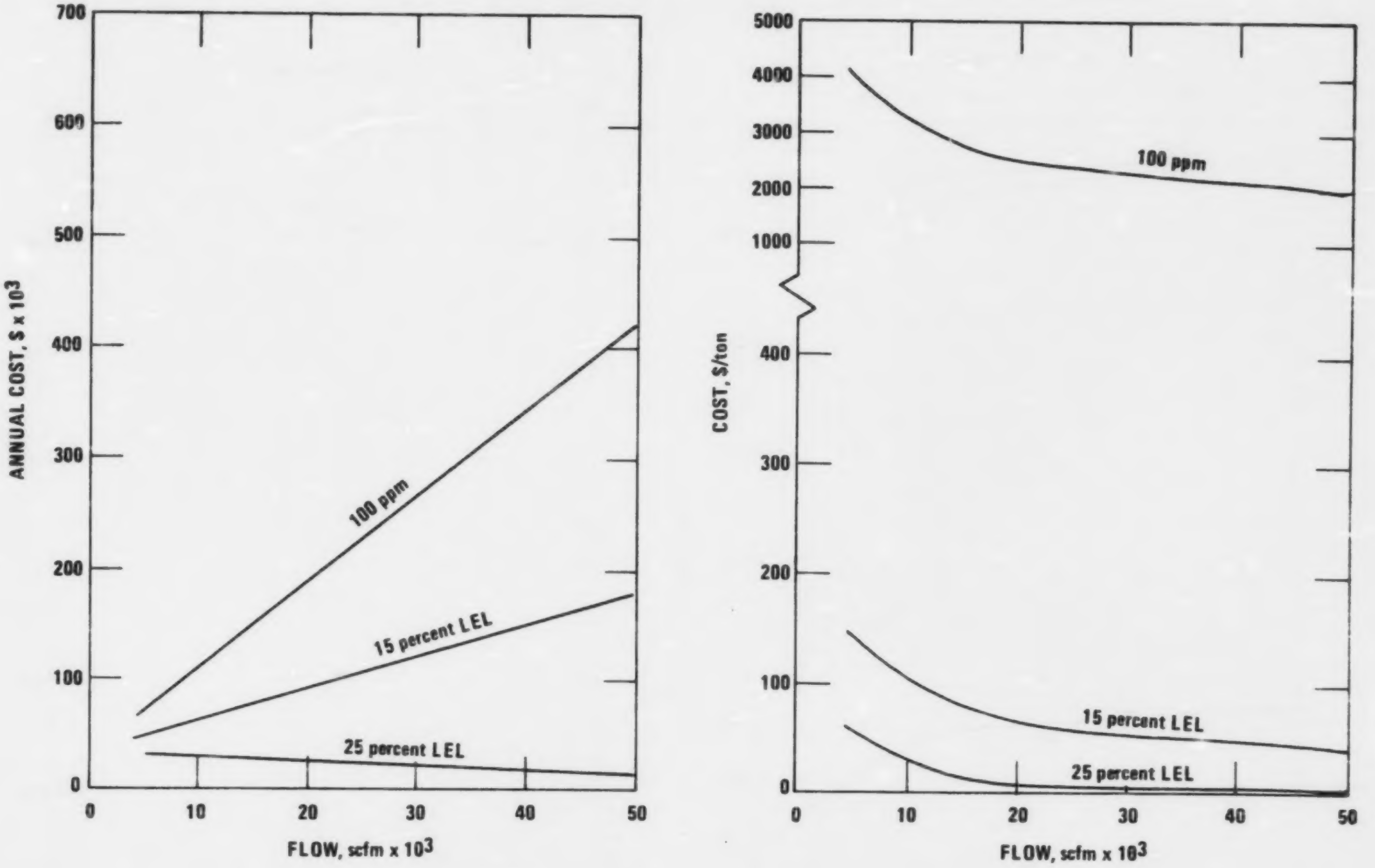

Figure 4-12. Annual cost and cost-effectiveness of direct flame incinerators (primary and secondary heat recovery - process temperature = 70 ^{o}F) - Case 3.

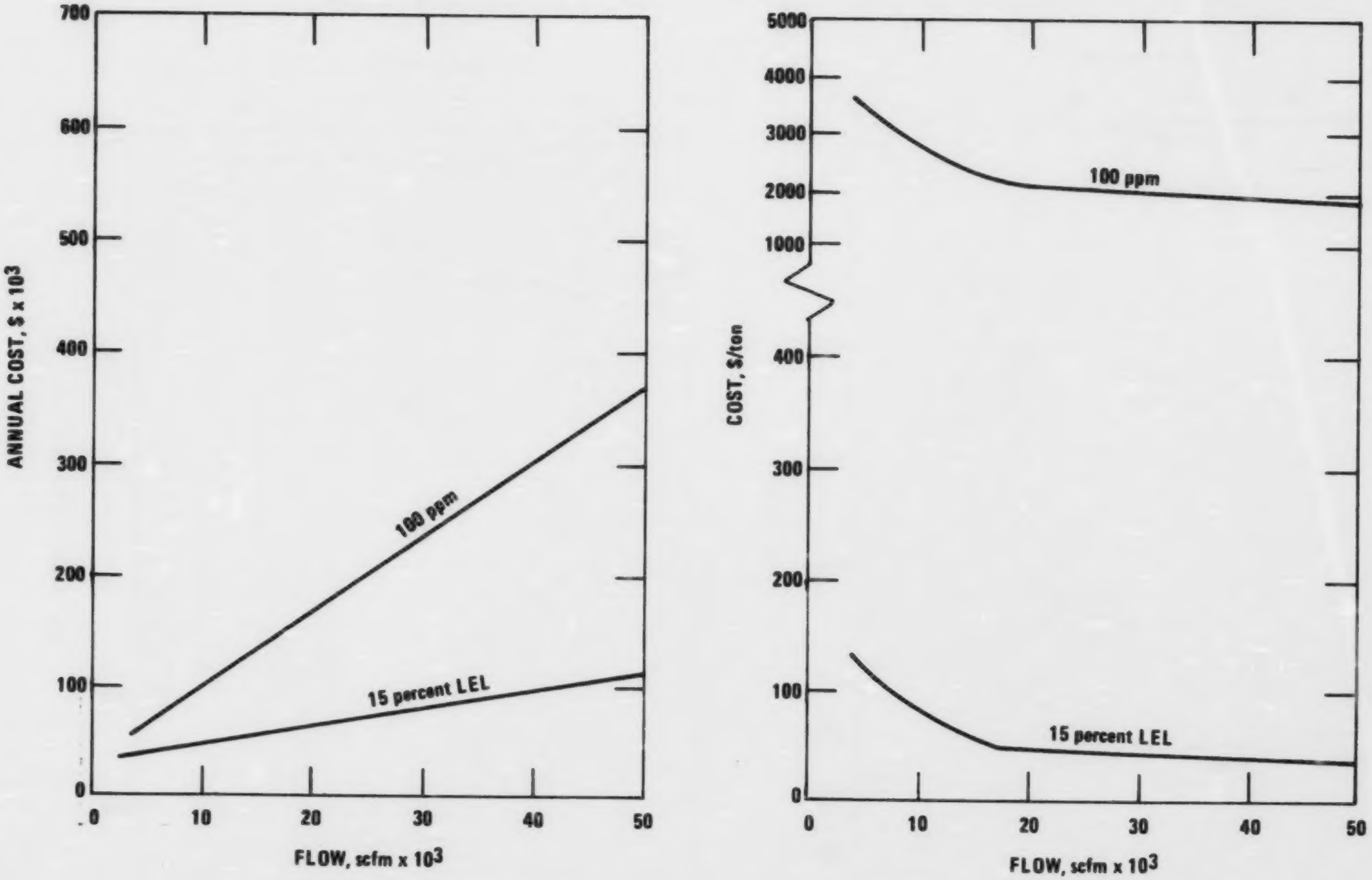

Figure 4-13. Annual cost and cost-effectiveness of direct flame incinerators (primary and secondary heat recovery - process temperature = 300 °F) - Case 3.

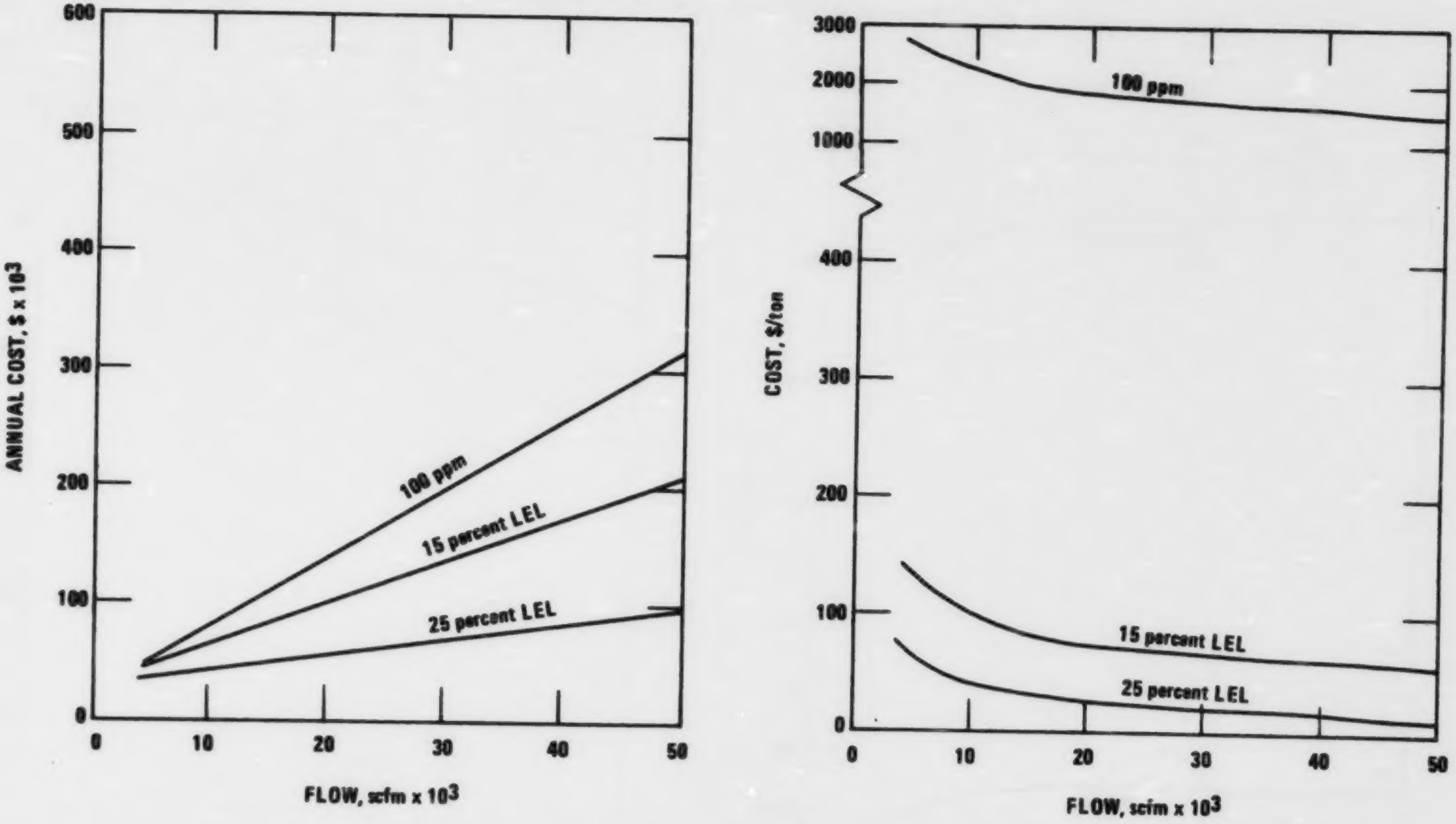

Figure 4-14. Annual cost and cost-effectiveness of catalytic incinerators (primary and secondary heat recovery - process temperature = 70 °F) - Case 3.

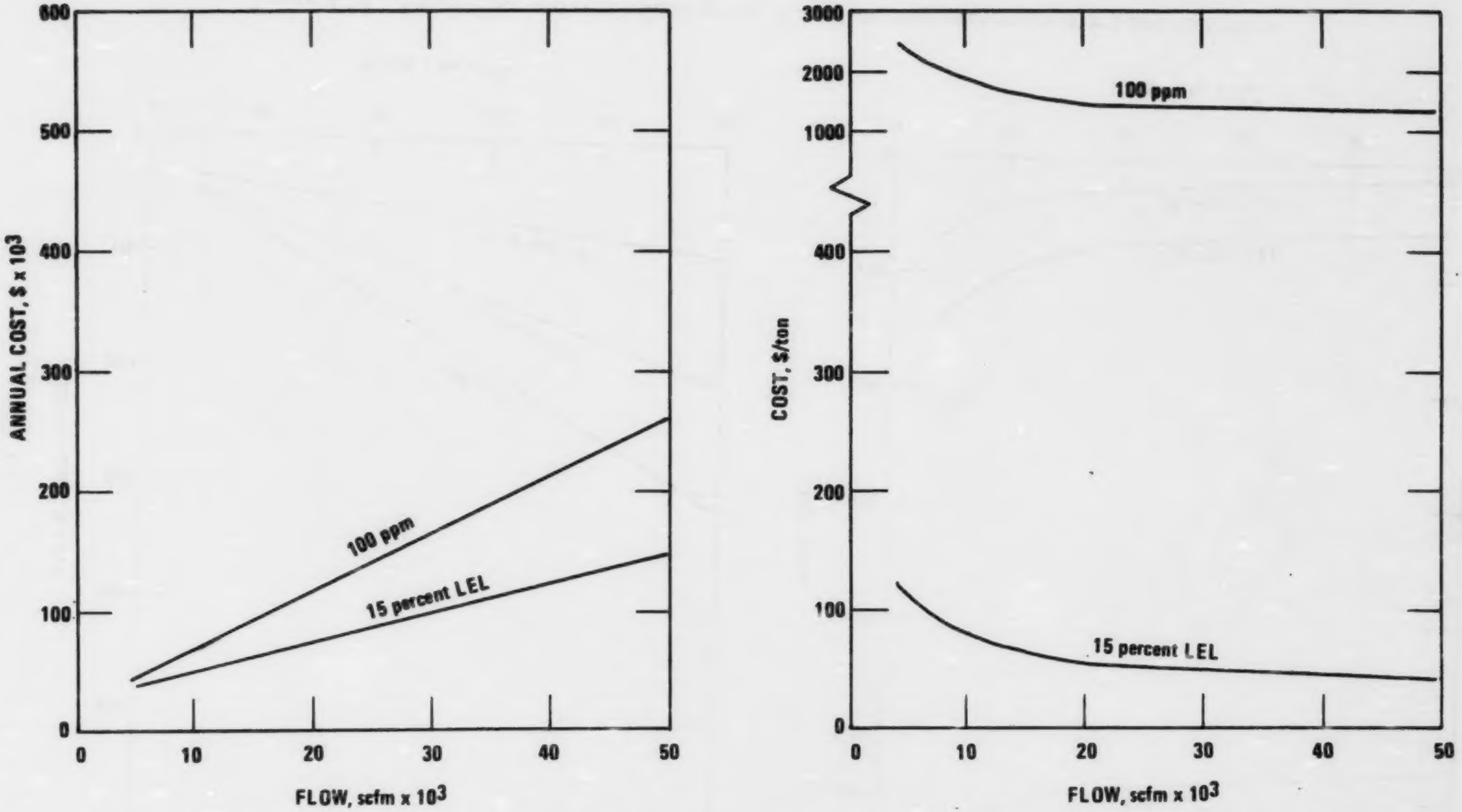

Figure 4-15. Annual cost and cost-effectiveness of catalytic incinerators (primary and secondary heat recovery - process temperature = 300 °F) - Case 3.

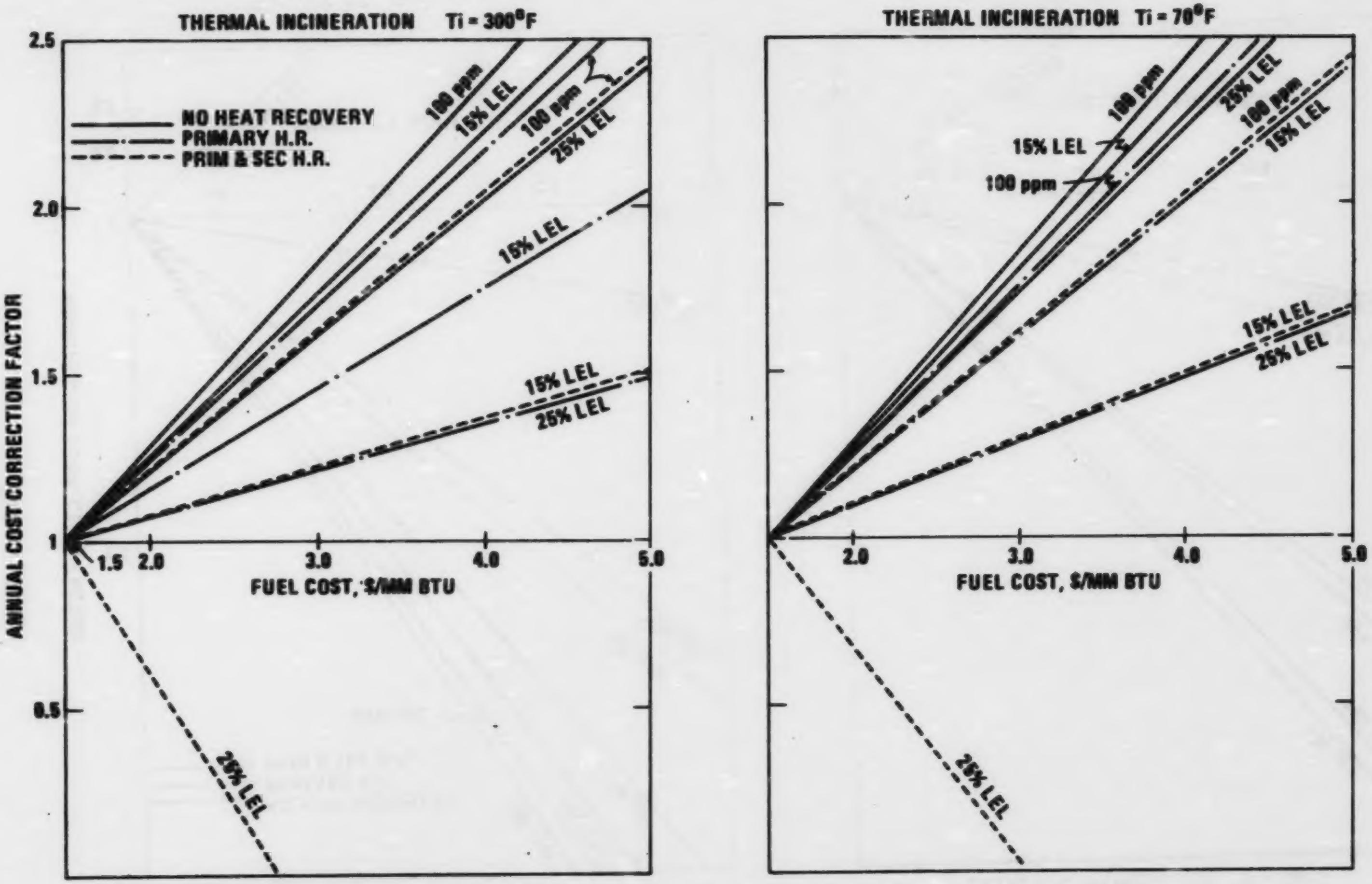

Figure 4-16. Factors to correct annual cost of thermal incineration for varying fuel cost.

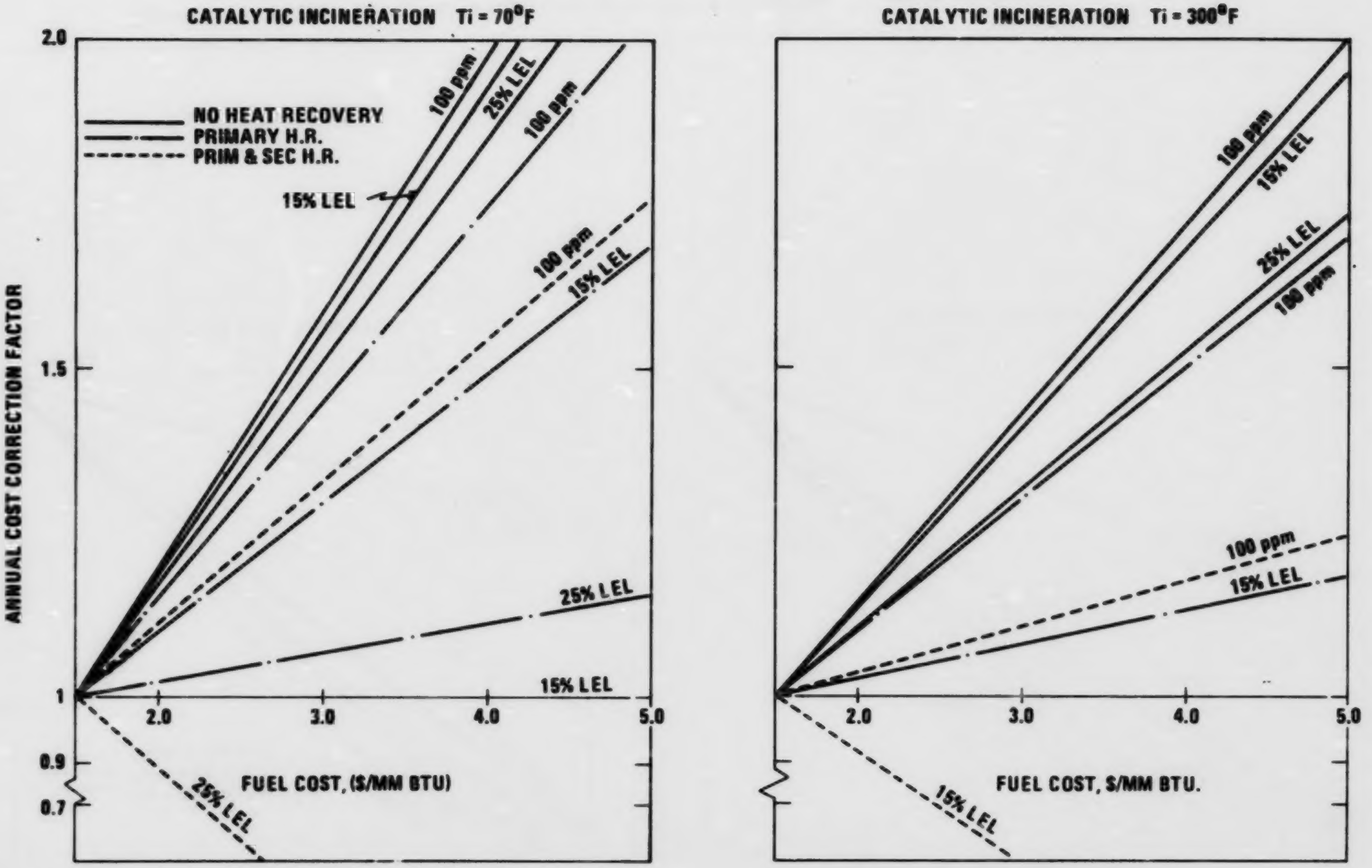

Figure 4-17. Factors to correct annual cost of catalytic incineration for varying fuel cost.

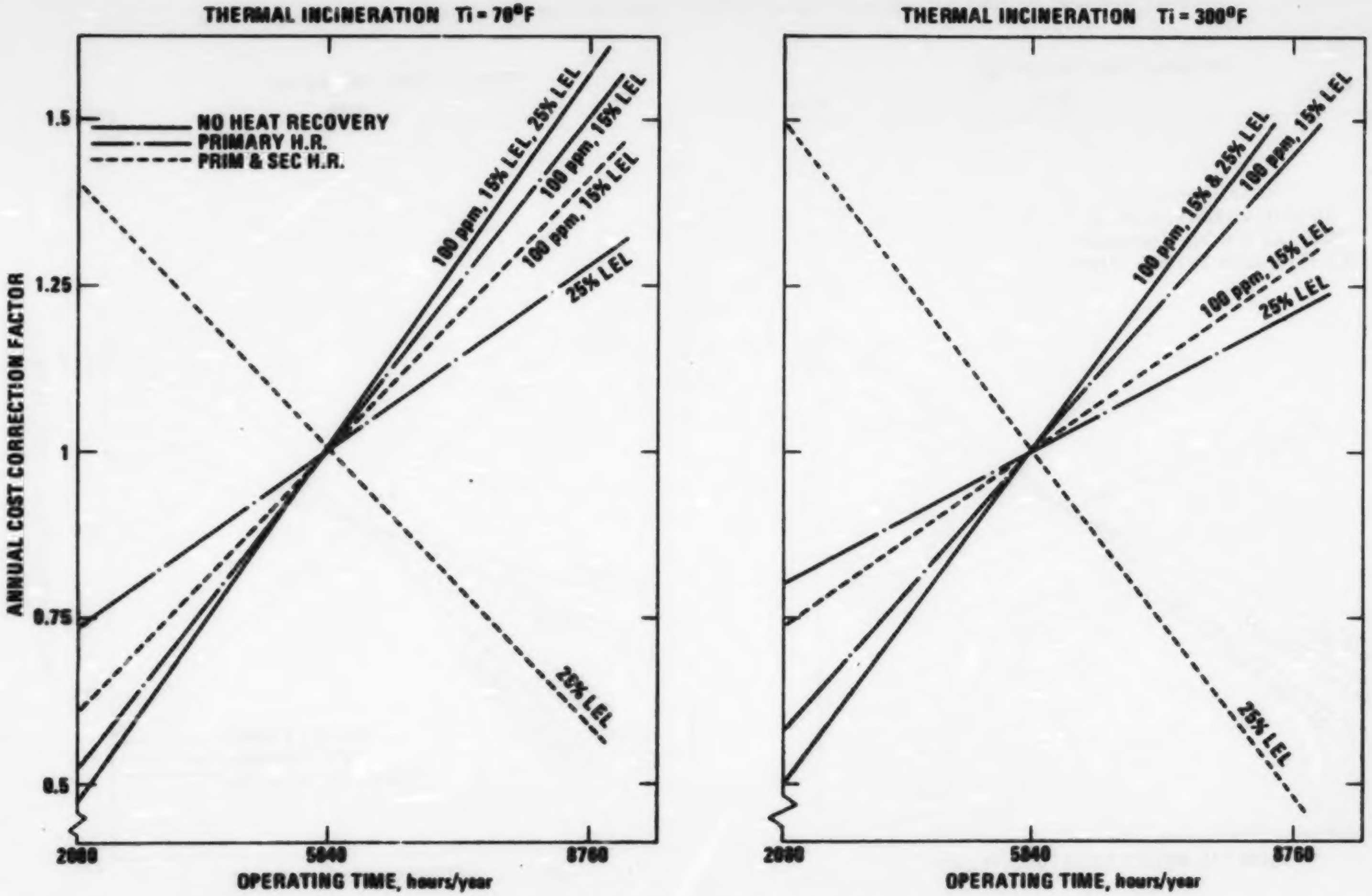

Figure 4-18. Factors to correct annual cost of thermal incineration for varying operating time.

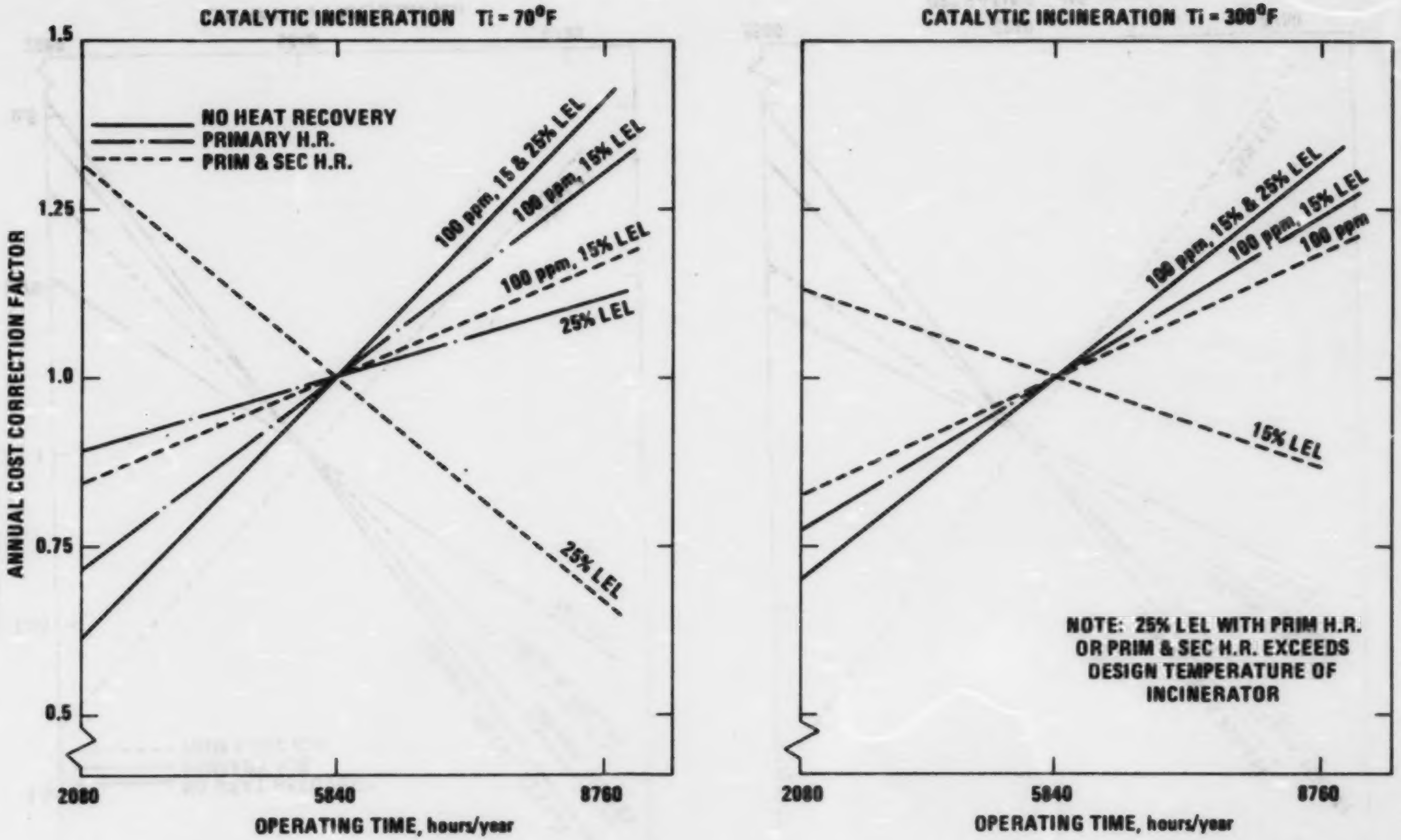

Figure 4-19. Factors to correct annual cost of catalytic incineration for varying operating time.

Table 4-4 INCREASE IN ANNUAL COST OF DIRECT FLAME INCINERATORS DUE TO RETROFIT DIFFICULTY FACTORS

Vapor Concentration	Process Temperature	Heat Recovery	Percent Increase in Annual Cost At Retrofit Difficulty Factor: 1.5	2	3
100 ppm	70°	None	2	5	9
15 percent LEL	70°	None	4	7	14
25 percent LEL	70°	None	5	10	20
100 ppm	300°	None	3	6	11
15 percent LEL	300°	None	4	8	16
25 percent LEL	300°	None	7	15	30
100 ppm	70°	Primary	4	9	18
15 percent LEL	70°	Primary	8	16	32
25 percent LEL	70°	Primary	17	33	66
100 ppm	300°	Primary	5	10	20
15 percent LEL	300°	Primary	10	20	40
25 percent LEL	300°	Primary	20	40	80
100 ppm	70°	Pri. & Sec.	8	16	32
15 percent LEL	70°	Pri. & Sec.	16	32	64
25 percent LEL	70°	Pri. & Sec.	80	160	320
100 ppm	300°	Pri. & Sec.	10	20	40
15 percent LEL	300°	Pri. & Sec.	25	50	100

Table 4-5 INCREASE IN ANNUAL COST OF CATALYTIC INCINERATORS DUE TO RETROFIT DIFFICULTY FACTORS

Vapor Concentration	Process Temperature	Heat Recovery	Percent Increase in Annual Cost At Retrofit Difficulty Factor: 1.5	2	3
100 ppm	70°	None	6	13	25
15 percent LEL	70°	None	6	13	26
25 percent LEL	70°	None	8	15	30
100 ppm	300°	None	8	16	33
15 percent LEL	300°	None	9	17	34
25 percent LEL	300°	None	11	22	43
100 ppm	70°	Primary	6	13	25
15 percent LEL	70°	Primary	11	22	45
25 percent LEL	70°	Primary	22	44	88
100 ppm	300°	Primary	10	20	40
15 percent LEL	300°	Primary	15	30	60
25 percent LEL	300°	Primary	16	33	65
100 ppm	70°	Pri. & Sec.	12	24	48
15 percent LEL	70°	Pri. & Sec.	18	36	72
25 percent LEL	70°	Pri. & Sec.	36	72	144
100 ppm	300°	Pri. & Sec.	14	28	56
15 percent LEL	300°	Pri. & Sec.	25	50	100

Three observations regarding catalytic incinerators are offered for those choosing between a catalytic and noncatalytic incinerator. First, a catalytic incinerator will probably oxidize any sulfur in the fuel to SO_3 which will subsequently form sulfuric acid mist. Therefore, it is recommended that only fuels that are essentially sulfur free, i.e., natural gas and propane, be used with catalytic incinerators. Second, the catalytic element may be blinded by any particulate matter in the exhaust gases to be incinerated; the blinding reduces effectiveness because the catalyst contact area has been decreased. Third, catalysts cannot operate above approximately 1200°F and still give reasonable service life (2 to 3 years). In general, catalyst manufacturers will limit their applications to streams with concentrations no higher than 25 percent of the LEL.

Primary heat recovery (preheat of the effluent from the oven before it enters the incinerator) reduces the fuel rate in the incinerator significantly regardless of inlet temperature or LEL condition. However, at the higher LEL concentrations, the requisite heat exchanger presents problems for both catalytic and noncatalytic incinerators. At the assumed 35 percent efficiency of the heat exchanger, the design limitations for the incinerators may be exceeded (for example, the catalytic unit may be forced to operate at temperatures greater than 1200°F, which would shorten the life of the catalyst). This problem can be solved by using a bypass around the primary heat exchanger, in effect creating a heat recovery unit of variable efficiency.

Annual control cost curves for incinerators with primary heat recovery are presented in Figures 4-7 and 4-10.

An important assumption used in developing the cost estimates for Case 3 is that all of the recovered secondary heat is utilized. Section 3.2.2 discusses the implications of this assumption.

4.2.2.2 Adsorption -- Whereas incineration relies on heat recovery techniques to offset annual operating cost, adsorption systems rely primarily on solvent recovery and/or heat recovery to offset annual operating cost. Many different configurations could be costed out. To simplify the analysis and presentation of results, this section is limited to carbon adsorptionsystems with solvent recovery, the system that is more commonly used.

Several assumptions were made in developing the cost estimates presented in this section. These basic assumptions are listed in Table 4-8. In addition to these assumptions, several assumptions were made when defining the control system before the cost analyses were initiated. The approach taken was to use Reference 2 as a source for such design information as horsepower requirements and water requirements for the various sized control systems. Where possible, assumptions for adsorption systems were chosen to be identical to assumptions for incinerators (see Table 4-3) to provide a direct cost comparison between adsorption systems and incinerator systems. The recovered solvent was assumed to be valued at (1) zero value, (2) $1.50 per million Btu based on using the recovered solvent as a fuel, (3) $0.85 per gallon for benzene and $0.465 per gallon for hexane based on selling the recovered solvent at its current market value.

The assumptions do not provide for any distillation equipment or water treatment facilities. If any water soluble compounds are encountered in the vapor, the costs will be increased considerably. The costs do not include

Table 4-8. ASSUMPTIONS USED IN DEVELOPING COST ESTIMATES FOR CARBON ADSORBERS

- Exhaust gases contain benzene and hexane (50/50 weight percent) mixture in air.
- Exhaust gas temperatures of 70, 170, and 375°F.
- Hydrocarbon concentrations of 100 ppm, 15 percent of the LEL and 25 percent of the LEL.
- Exhaust gas flow rates of 1,000, 10,000, 50,000 scfm.
- Fuel costs of $1.50/million Btu.
- Electricity at $0.03/kw-hr.
- Activated carbon at $0.68/lb.
- Water at $0.04/thousand gallons.
- Steam at $2/thousand lb.
- 5-year life of activated carbon.
- Adsorber operating at 100°F.
- Market value (December 1975) of benzene = $0.85/gallon; market value (December 1975) of hexane = $0.465/gallon.
- Normal retrofit situation.
- Direct labor assessed at 0.5 hr/shift x 730 shifts/yr x $8/hour = $2920/yr.
- Annual maintenance, taxes, insurance, building overhead, depreciation, and interest on borrowed money taken as 25 percent of capital investment.
- Operating time = 5840 hr/yr.

any particulate removal equipment. Compounds which are difficult to adsorb or desorb, if present, will also add considerably to the installed and operating costs.

Installed cost of adsorbers -- Capital cost for adsorption systems designed to recover the solvent is given in Figure 4-20 Based upon Figure 4-20, the unit capital costs for two gas flow rates are given in Table 4-9.

For a given gas flow rate in Table 4-9, the higher unit costs are for adsorption of gases at 25 percent of the LEL and the lower unit costs are for concentrations of 100 ppm.

Table 4-9. UNIT CAPITAL COST FOR CARBON ADSORPTION SYSTEMS

Gas flow rate, scfm	Control cost, $/scfm
5,000	30 - 36
30,000	18 - 21

Annual control cost for adsorbers -- Figures 4-21 through 4-23 are given to illustrate the annual costs of carbon adsorption systems over a representative size range. These figures and Table 4-10 illustrate the importance of the value of the recovered solvents.

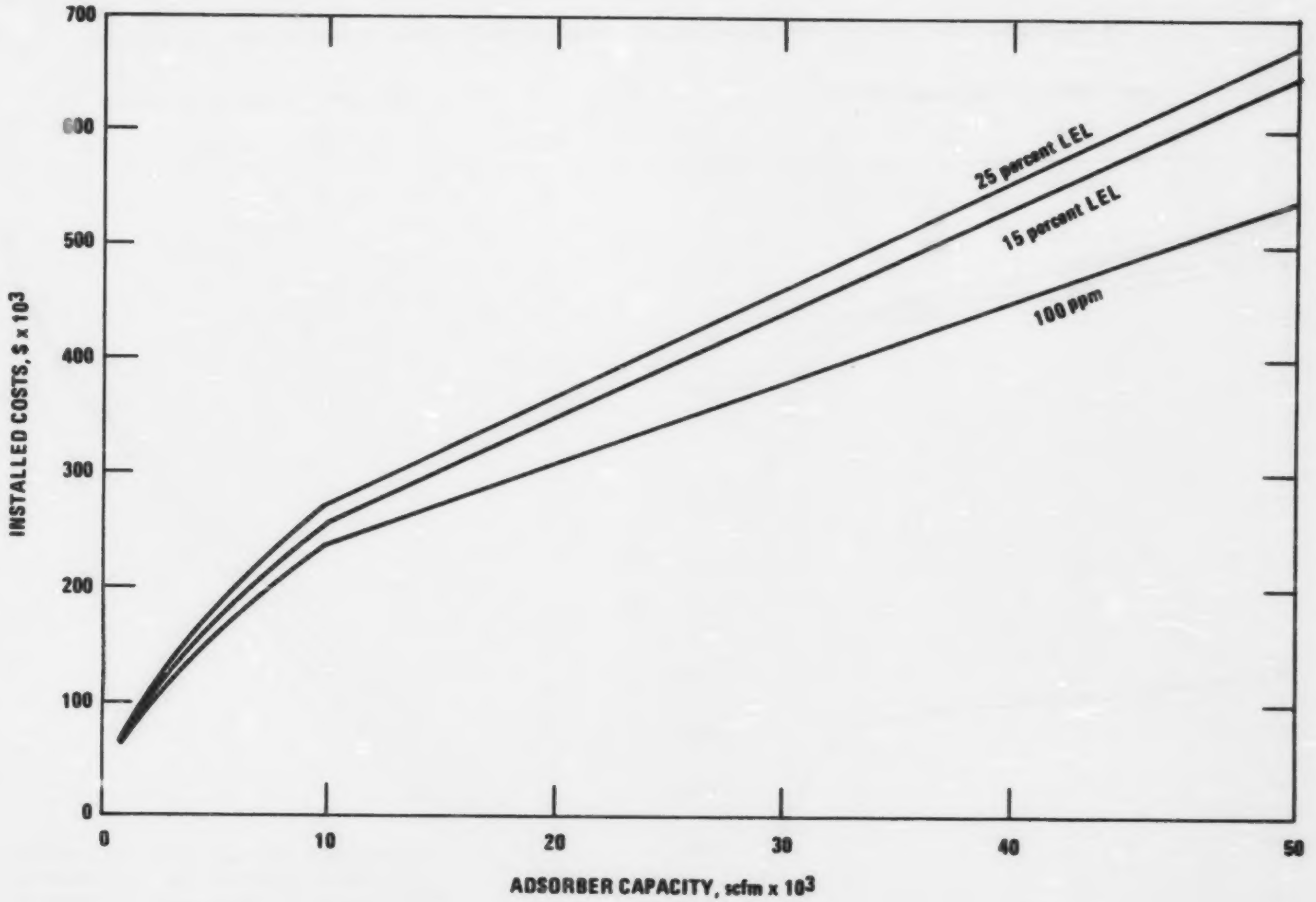

Figure 4-20. Estimated installed adsorption system cost.

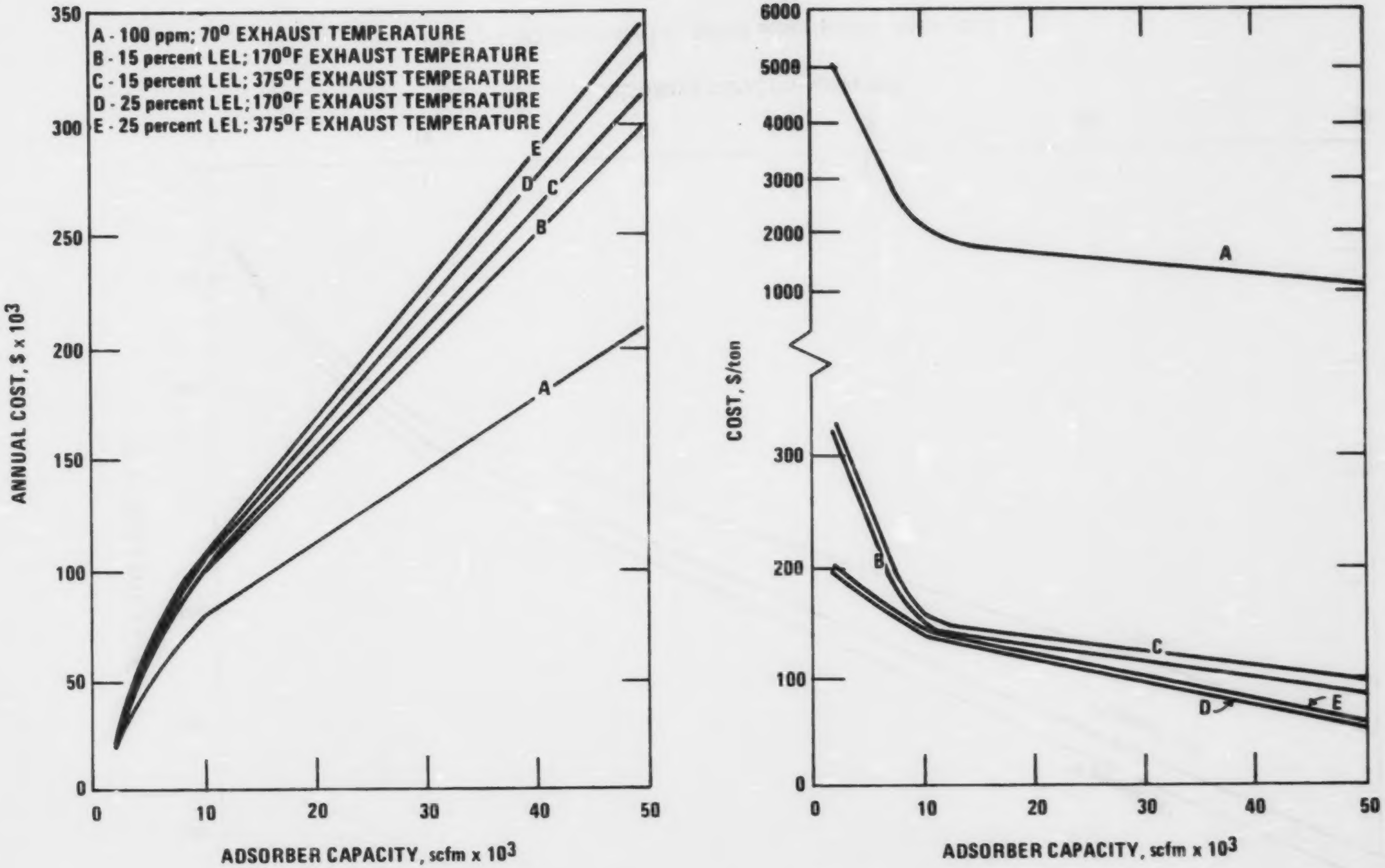

Figure 4-21. Annual cost and cost-effectiveness of carbon adsorption systems (no credit given for recovered solvents).

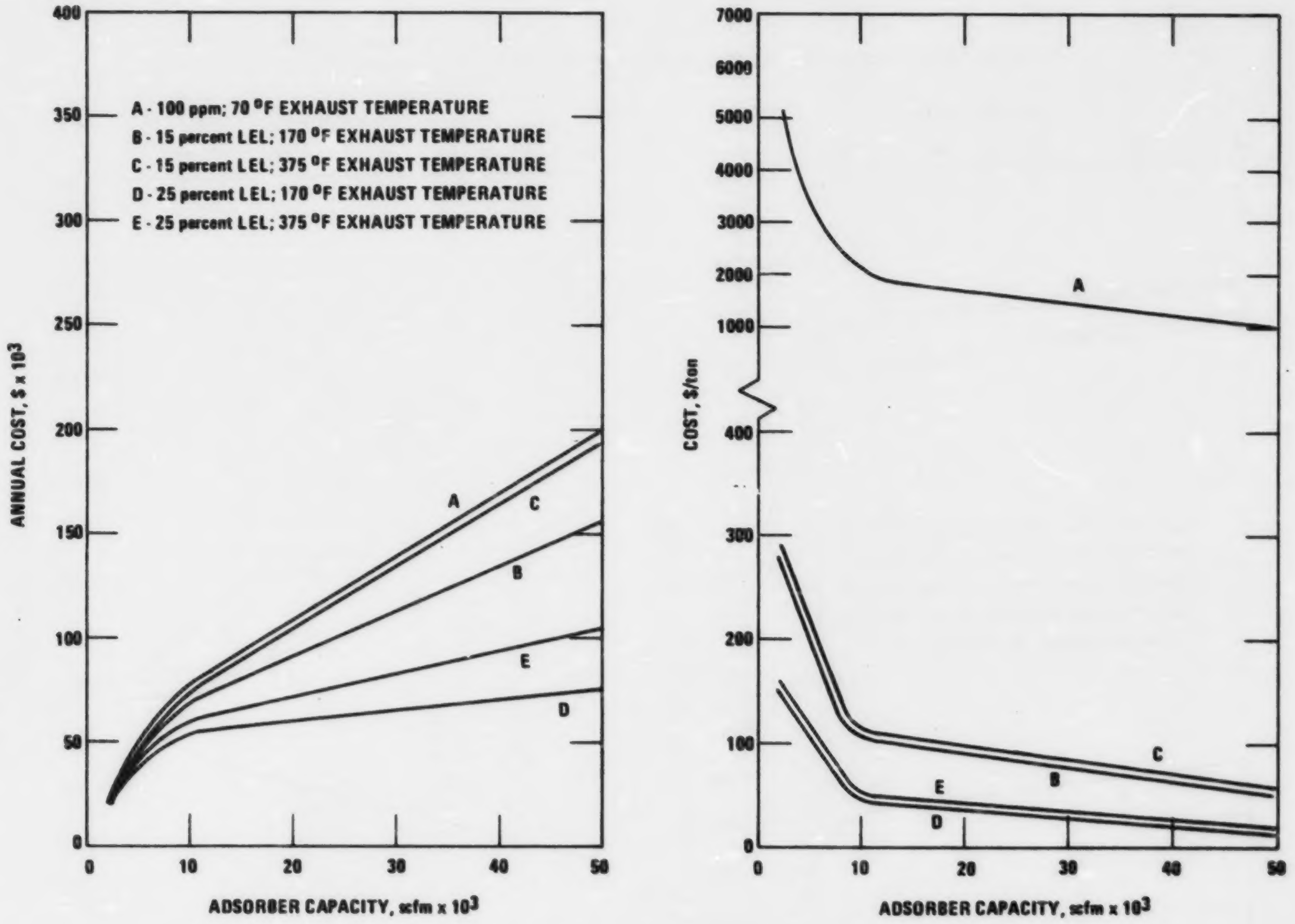

Figure 4-22. Annual cost and cost-effectiveness of carbon adsorption systems (recovered solvent credited at fuel value).

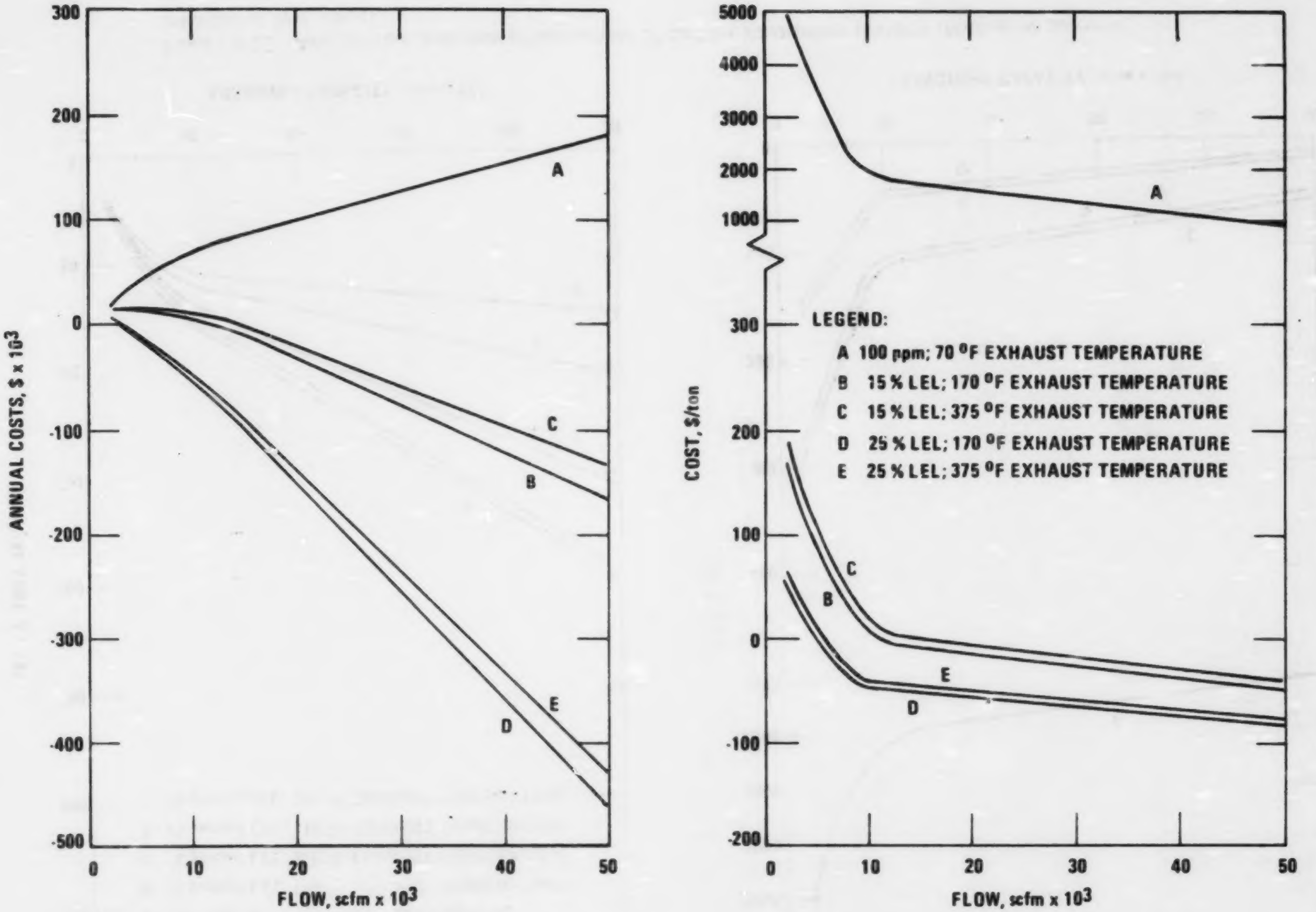

Figure 4-23. Annual cost and cost-effectiveness of carbon adsorption systems (recovered solvent credited at market chemical value).

Table 4-10. ANNUAL COST FOR CARBON ADSORPTION SYSTEMS

Value of recovered solvent	Annual cost, 10^3 $	
	5,000 scfm	30,000 scfm
No value	$47^a - 65^b$	$145^a - 230^b$
Value = fuel value	$35^b - 47^a$	$65^b - 140^a$
Value = market chemical value	$(15)^b - 40^a$	$(255)^b - 130^a$

[a] Low concentrations.

[b] High concentrations; parentheses indicate a net profit.

4.2.2.3 Cost Comparisons, Incineration Versus Adsorption -- Based upon the cost analysis in this section, the following conclusions are indicated:

1. For control of low hydrocarbon concentrations (approximately 100 ppm), carbon adsorption is more economical than incineration if there are no water soluble compounds in the vapor, no compounds which are difficult to adsorb or desorb, and no particulate matter.
2. For control of high hydrocarbon concentrations (approximately 25 percent of the LEL), carbon adsorption is more economical than incineration only if recovered solvent can be credited at market value and none of the above-mentioned types of material are encountered.
3. Incineration with primary heat recovery is more economical than adsorption at high concentrations if no value is given for recovered solvents.

4.3 REFERENCES FOR CHAPTER 4

1. Interim report on cost of incineration. Combustion Engineering, Air Preheater Division, Wellsville, New York. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C., under Contract No. 68-02-1473. December 1975.

2. Hydrocarbon Pollutant Systems Study. Vol. II. MSA Research Corp. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C., under Contract No. EHSD 71-12. Publication No. APTD-1500. January 1973.

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5.0 APPROACHES TO DETERMINATION OF TOTAL "NONMETHANE" HYDROCARBONS

5.1 Summary

No single, practical emission measurement method currently exists that can be generally used to determine total nonmethane concentrations in all situations. If used selectively, however, several hydrocarbon sampling and analytical techniques that yield acceptable results are available for specific applications. This section briefly explains each of these techniques and provides application guidelines. Supplementary measurements needed to determine an emission rate are also suggested. For this section "hydrocarbons" is used interchangeably with "volatile organics".

5.2 Introduction

Where applicable, a material balance is the most accurate measurement technique available. The technique relies on the fact that what goes into the process must exit the process, unless chemical change occurs. It is useful for such sources as spray booths and low temperature ovens where control is by carbon adsorption. The solvent content for coatings can easily be determined and the amount of solvent recovered can be accurately measured. For chemically reactive coatings, e.g. two component coatings, correction for the reaction products is necessary. Some problems can occur if separation of evaporation quantities is necessary, e.g., for spray booths and following ovens. In such cases it would probably be necessary to measure the emission from at least one of the exhaust streams to determine the proper apportionment of emissions.

For those cases where a material balance can be made, the recommended approach is for the sources to be required to keep records of solvent used (including diluent and cleaning solvent) and solvent recovered. A one week check by the control agency could be used to verify the plants record-keeping system.

Source evaluation by emission measurement can be applied when it is not possible to generate emission values of sufficient accuracy through a material balance, or when stack gases have been oxidized or otherwise affected to an unknown extent. Emission measurement methodology involves two separate but related steps: sample collection and sample analysis. Before using any specific test method, however, the question of whether the collection and analytical techniques will satisfy the true intent of the hydrocarbon emission standard must be resolved.

Although the definition of any pollutant in a desired or proposed emission standard is normally the point of reference for designing the emission measurement method, it must be recognized that the measurement method used can modify the pollutant "definition." Therefore, to satisfy the true intent of the emission standard, attention must be given to the proper selection of measurement methodology and to the elimination of vagueness in the specifications of the selected method. Consider for a moment a definition of nonmethane hydrocarbons as "those hydrocarbons, methane excepted, which exist in the gaseous state or behave as a gas at the point of measurement." The words "behave as a gas" are important from a collection standpoint, because it may not be possible to separate the gaseous from the particulate hydrocarbons without inducing a mechanism that shifts the original gas/particulate ratio.

For example, if a sample collection method specifies a glass wood plug or similar filter in the gas sample probe to prevent particulate hydrocarbons from reaching the sample container, gaseous hydrocarbons might adsorb on the filter, or they might condense on particulate hydrocarbons or other particulate condensation nuclei. Particulate hydrocarbons initially entrapped on the filter could, on the other hand, vaporize during the course of sampling. When sampling occurs, where acids are present, such as at an incinerator outlet, the filter could serve as a site for reactions between acids and hydrocarbons. Moreover, by not specifying that the sample probe is to be heated to stack temperature, an additional question could be raised as to the possible loss of sample resulting from condensation in the probe.

Analytical requirements should also be indicated in the definition of nonmethane hydrocarbons. For example, a definition that states "...measured on a carbons basis..." specifies that all the carbon atoms present in the sample that result from nonmethane hydrocarbons are to be counted. Omission of this clause would imply that the analysis method must report the entire mass of the nonmethane hydrocarbon compounds.

Because of variations in the makeup of the hydrocarbons emitted, each process tested must be individually evaluated to ensure that the collection and analytical methods employed are consistent with the definition of nonmethane hydrocarbons.

5.3 Measurement Approaches

General requirement for obtaining valid air pollution measurements are covered quite well in the literature[1,3] and will not be restated here. The currently employed hydrocarbon source measurement techniques are limited to the "extractive" classification, which means the gas must be withdrawn from the source before it can be analyzed.

Normally, process off-gas is extracted at the centroid of the stack or duct, except when there is reason to suspect that the hydrocarbon concentration varies within the stack cross section. In that event, the sample must be obtained by a procedure known as traversing, that is the sample must be obtained from the centroids of a number of equal areas within the cross section. (The number selected is in direct proportion to the expected degree of irregularity in the exhaust gas.)

Variations in gas concentrations are most often encountered where relatively quiescent zones exist in the stack cross section. These zones are usually revealed by a velocity traverse. If several ducts that serve different processes or vent noncontinuous operations are manifolded together, however, insufficient gas mixing could result in unpredictable concentration variations -- the presence of which would not be disclosed by a velocity traverse. Either of the above situations are best revealed by traversing the cross section with a continuous-response hydrocarbon detector. In addition, persons conducting the test must be familiar with the processes served by the stack to assure representative sampling of the emissions.

Depending on the requirements of the emission standard, either a grab (instantaneous) sample or an integrated sample (a sample collected at a rate proportional to the stack flow rate for a specified time period) may be taken. Three consecutive samples are normally collected for each test.

If the mass emission rate is to be measured, simultaneous or near simultaneous measurements of stack flow rate are required. Unless the stack gas mixture is known (air, for example), its molecular weight must be determined. As most analytical techniques are on a wet basis, the water content of the exhaust must also be measured to correct flow rates and hydrocarbon concentrations to standard conditions. EPA Methods 2,3, and 4, respectively, will normally suffice.[4]

If the emission concentration varies and the emission standard is a time-averaged value, grab samples may be taken in sufficient quantity and spread over a given time period to yield an average value. When the stack flow rate also varies, it will have to be measured at the time each grab sample is taken in order to proportion the results. Grab samples may be analyzed directly, or be held for subsequent recovery and analysis. Integrated gas samples may be collected without alteration, or the hydrocarbons can be concentrated with a sorbent. If the emission concentration is suspected to vary erratically with time, it is best to use the integrated sample approach thus reducing the total number of samples to be analyzed. In some situations. a continuous hydrocarbon detector can be integrated into the sampling system with its data averaged either manually or automatically over a given time period.

The next two portions of this section are devoted to explanations and discussions of sampling and analytical techniques that show promise for the determination of total nonmethane hydrocarbons. These techniques can, except as noted, be combined in a variety of ways to yield an emission measurement. The best combination for a particular source category will depend on the intent of the regulation or emission standard in question.

5.4 Sampling

General sampling techniques and precautions have been extensively reported;[2,3,5] those most suited to collection of total nonmethane hydrocarbons are discussed below.

Activated Carbon Adsorption -- First investigated for use as an air sampling method by Kupel et al.,[6] an activated carbon collection device (Figure 5-1) was further examined by Mueller and Miller in 1974.[7] Figure 5-1 shows a typical sample device. Once adsorbed on the activated carbon, hydrocarbons are subsequently desorbed with a solvent--usually carbon disulfide. The hydrocarbon sample, now a liquid, is then analyzed by a detector that is insensitive to the solvent.

Advantages of the carbon adsorption tube are:

1. Small sample quantities are collected.
2. Leaks are less likely to occur, in comparison with bag samples.
3. Analysis of each sample can be repeated several times because only a few milliters of the solution are required.

Disadvantages include:

1. Gas temperature must be below 125°F for adsorption to be effective; precoolers are often required.
2. Moisture in the stack gas may condense and plug the carbon bed.
3. A total gas sample is not collected, so hydrocarbon "breakthrough" must be prevented. Because a second carbon section is needed in each tube to demonstrate collection efficiency, each sample becomes two samples, thus doubling the number of analyses required.
4. Collection efficiency for noncondensible and some volatile organics is poor.[7]
5. Sample desorption efficiency is poor for some volatile organics, particularly polar compounds.[7]
6. Organic compounds could be displaced from carbon by more readily adsorbed gases.[7]
7. The technique is not adaptable to total combustion analysis.

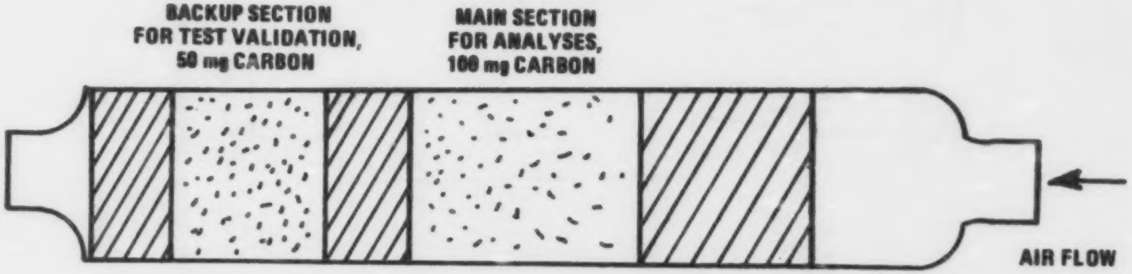
BACKUP SECTION
FOR TEST VALIDATION,
50 mg CARBON
MAIN SECTION
FOR ANALYSES,
100 mg CARBON
AIR FLOW

Figure 5-1. Carbon-filled tube employed to trap solvent vapors.[7]

Universal Collector -- The Universal Collector described by Isbell[8] also employs activated carbon, but only to collect the more volatile organic compounds (see Figure 5-2). A preadsorber of Tenax GS is used to collect hydrocarbons that are difficult to desorb from activated carbon.

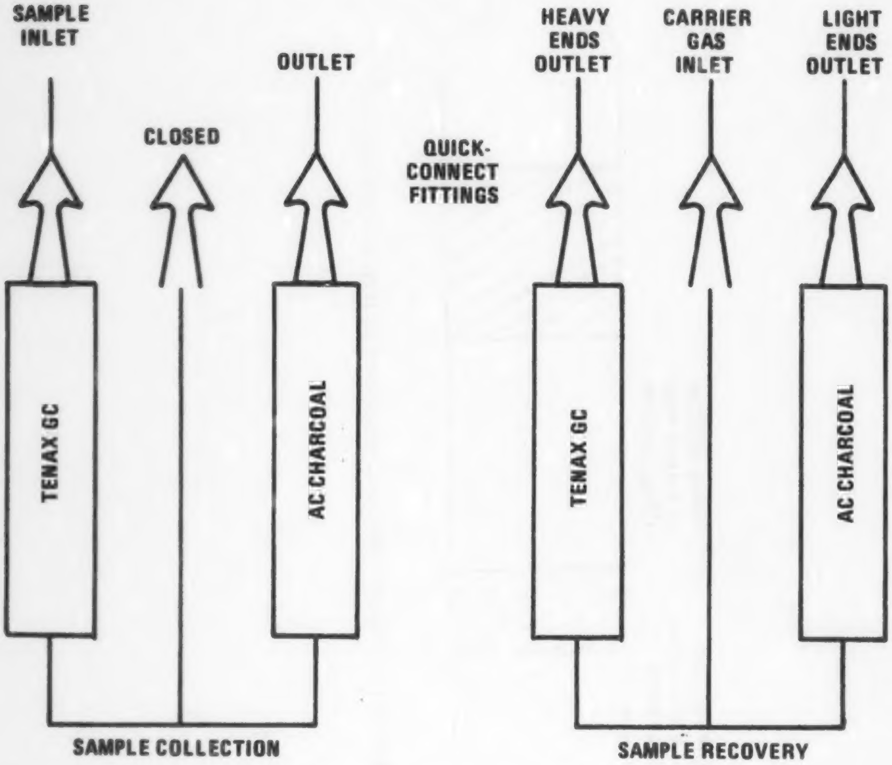
SAMPLE INLET
CLOSED
OUTLET
QUICK-CONNECT FITTINGS
HEAVY ENDS OUTLET
CARRIER GAS INLET
LIGHT ENDS OUTLET
TENAX GC
AC CHARCOAL
TENAX GC
AC CHARCOAL
SAMPLE COLLECTION
SAMPLE RECOVERY

Figure 5-2. Schematic diagram of universal collector.[8]

The adsorbers are maintained at or below ambient temperature during sample collection. Recovery is obtained by raising the temperature to approximately 200°C and flushing the adsorbers with a carrier gas.

Advantages of the Universal Collector over activated carbon alone are:

1. Sample collection and recovery efficiencies are improved.
2. The method is adaptable to total combustion analysis.
3. Sample recovery prodedures are simplified.

Disadvantages include:

1. Two collectors in series must be used to demonstrate good collection efficiency.
2. Operating temperature during sampling affects collection efficiency. Efficiency is best at low temperature but if the temperature is too low, water condensation may plug the device.
3. Because extensive collection and recovery efficiency data are lacking, source components should be checked before the procedure is used.
4. Only one analysis can be made of each sample.

Cold Trap/Evacuated Cylinder - Condensable organics can be concentrated with a cold trap, which normally consists of a piece of stainless steel tubing immersed in a refrigerant. Midget impingers, however, both with and without tips, can be used in place of the tubing. A pump or an evacuated cylinder can be used to move the sample gas, if necessary. If a pump is used, the cylinder must be teed-in between the second cold trap and the pump. Collection occurs when the pollutant vapor is sufficiently cooled to condense and deposit on the interior surfaces of the trap. Figure 5-3 is a generalized schematic of the sample system described by Gadomski et al.[9]

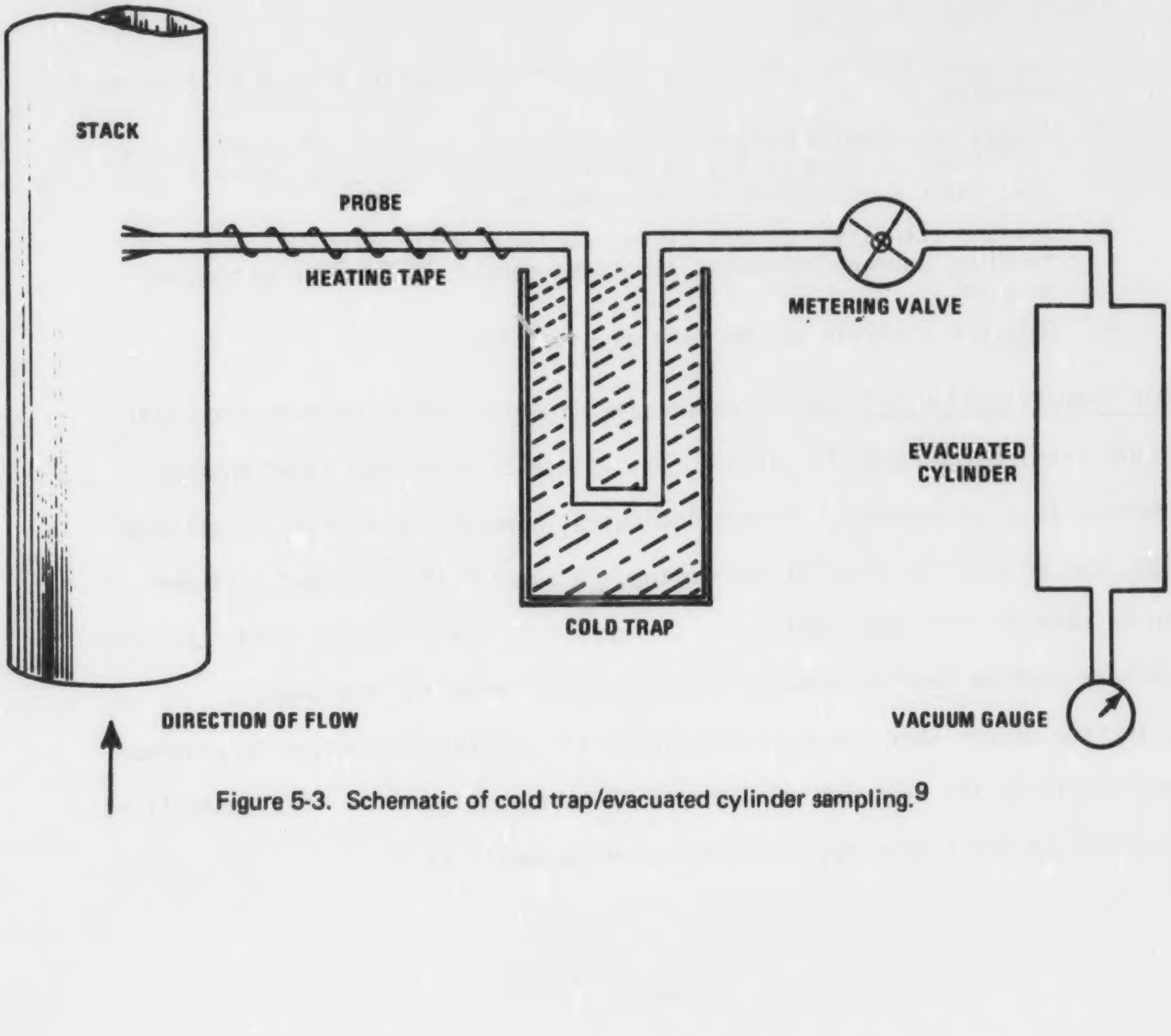
STACK
PROBE
HEATING TAPE
METERING VALVE
EVACUATED CYLINDER
COLD TRAP
DIRECTION OF FLOW
VACUUM GAUGE

Figure 5-3. Schematic of cold trap/evacuated cylinder sampling.[9]

Six inches of glass wool in the tubing immediately preceeding the metering valve prevents condensation carryover into the evacuated cylinder. Both the trap and the cylinder are analyzed for hydrocarbons.

Advantages of the sampling system are:

1. Collection efficiency should approach 100 percent because the device is a total gas sampler. (A total sample is not collected if a pump is used; collection efficiency must then be demonstrated by using a second cold trap placed in series with the first.)
2. If probe heating is not required, no electrical devices are required at the stack sample site.
3. No restrictions are made on the analytical technique(s) used.

Disadvantages include:

1. If condensible organics are carried into the cylinder, recovery may be incomplete.
2. Water in the stack gas may cause the cold trap to freeze. This difficulty may be avoided if the gas first passes through an impinger with the tip removed.
3. Only one analysis per sample can be made.
4. Proportional sampling is difficult if the cylinder vacuum is the sole stack gas withdrawal force.
5. Immersion of traps into refrigerant prior to sampling is accompanied by a lowering of internal pressure and a corresponding influx of gas must be taken into account when calculating sample volume.[10]

Syringe or Purge Flask - Relatively simplified grab samples can be collected with either glass syringes or purge flasks. If condensation problems are expected, either may be preheated with heat tape and maintained at an elevated temperature during the short sampling period with an insulated casing. Although the syringe is obviously a manual technique, the purge flask can also be manually operated with a rubber, one-way squeeze bulb. After it has been repeatedly flushed with stack gas, the syringe or purge flask is allowed to equilibrate to stack pressure before it is sealed. The syringe is difficult to leak check, but the purge flask is not. If the volume of the purge flask is large relative to the quantity of gas required for analysis, several analyses may be performed on the same flask before the pressure is appreciably decreased. On the other hand, the syringe is normally exhausted by one analysis. If sample adsorption on the walls of either device is appreciable, sample recovery may be enhanced by using a heat tape to raise the temperature.

The chief advantages of both techniques are:

1. They are least expensive of hydrocarbon sampling techniques; no reagents are required.
2. Electrical devices are not required at the sampling site, which is a safety consideration at sites where the atmosphere may be explosive.
3. Collected samples are suitable for various analytical techniques.

Disadvantages include:

1. It is difficult to detect leaks and perform leak checks on a syringe.
2. Multiple samples are required for time-averaged emission determinations.
3. It may be difficult to obtain repeatable analyses with identical samples unless sample recovery techniques are automated.

Collapsible Plastic Bags - Collapsible plastic bags have been used to collect integrated gas samples for several years. EPA Method 3 employs a flexible bag for samples to be analyzed for carbon dioxide, excess air, and dry molecular weight.[4] More recently, EPA has suggested that Tedlar® bags be used to collect samples for measurement of vinyl chloride emissions.[11]

The sampling train (see Figure 5-4) is intended to be used on stack exhausts having a relatively low moisture content, because water condensation

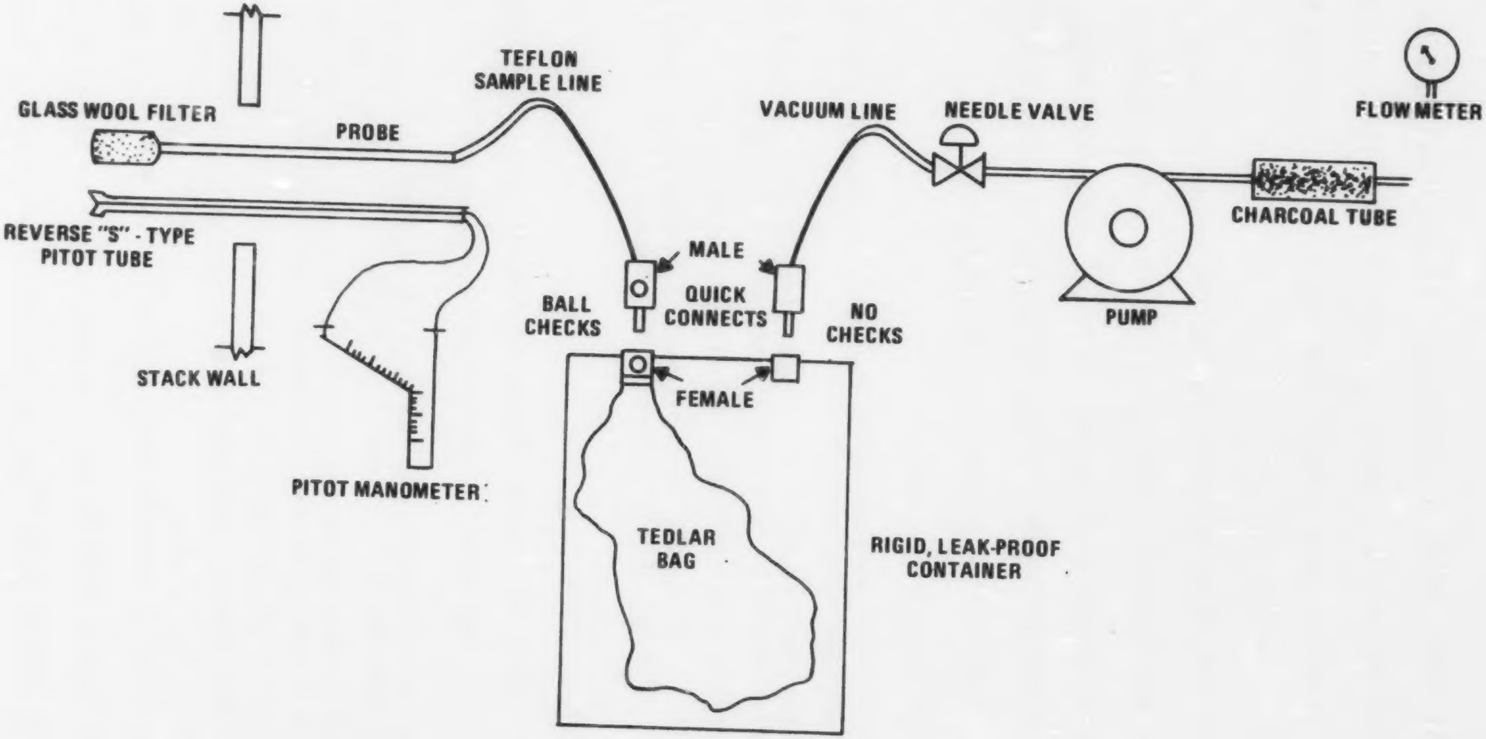
TEFLON
SAMPLE LINE
GLASS WOOL FILTER
PROBE
VACUUM LINE
NEEDLE VALVE
FLOW METER
CHARCOAL TUBE
REVERSE "S" - TYPE
PITOT TUBE
MALE
QUICK
CONNECTS
BALL
CHECKS
NO
CHECKS
PUMP
STACK WALL
FEMALE
PITOT MANOMETER
TEDLAR
BAG
RIGID, LEAK-PROOF
CONTAINER

Figure 5-4. Integrated bag sampling train.11

could affect the hydrocarbon concentration. If water condensation is a problem, predilution of the stack gas at a constant rate with clean dry air often has been suggested as a remedy. The bag must be subjected to a rigorous leak check before use.

Tedlar® has been shown to be a superior bag material,[12] but aluminized Mylar® may work equally well. Generally, any bag sample should be analyzed within 24 hours to minimize adsorption losses.[11] Other techniques for minimizing losses would include increasing the bag size (maximizing the volume/area ratio) and predonditioning the bag with sample gas.

Advantages of bag samples are:

1. Because a total air sample is provided, collection efficiency should approach 100 percent.
2. Sample recovery requires no intermediate procedure; the line is merely connected to the analyzer.
3. The quantity of each sample permits many reanalyses.
4. The quantity of sample is sufficient to serve other purposes, such as odor threshhold determinations.[12]

Disadvantages include:

1. The bag cannot be readily heated to enhance sample recovery.
2. Higher molecular weight compounds have a tendency to adsorb on bag walls.[10]
3. The size of the sample and the rigid container may create problems. As with any sample, it should be protected from sunlight.
4. Bags have a greater tendency to develop leaks than any other sampling device; frequent leak checks are mandatory.
5. The cost is high, relative to other sampling devices.
6. Some hydrocarbon solvents may react with the bag.[10]

Sample Direct to Analysis - As the name implies, this technique reduces the detainment of the sample from the point of extraction to the point of analysis to a minimum. The sample flows from the stack through a sample conditioning system (normally referred to as the interface system) to the hydrocarbon detector. Care must be taken to see that the sample interface system does not alter the hydrocarbons to an unknown degree. Its operation is best checked by periodically introducing a gas of known hydrocarbon concentration at the sampling probe. The previously calibrated analyzer is then monitored to verify attainment of the expected response.

The degree of complexity of an interface system may vary from the extreme of simply transporting a portion of the stack gas from the stack to the analyzer to the extreme of cooling or heating, filtering, drying, concentrating or diluting, and reacting the stack gas. Application of any of these steps are acceptable, provided the nature and extent of their occurrence is known.

Some advantages of direct analysis are:

1. Time-related degradation phenomena are elimianted.
2. The amount of sample equipment is reduced.
3. The use of a permanent or semipermanent setup reduces the frequency of leak checks.
4. The rapid availability of data may be useful for process control.

Disadvantages include:

1. It is not always possible to provide on-site analytical requirements.
2. The method requires a portable or semiportable analyzer, which may be an added expense.
3. Taking the analyzer to the source means it can only be at one source at a time, whereas a laboratory-situated analyzer could rapidly analyze samples from several sources.

5.5 Analysis

The means of detecting hydrocarbon gases, either directly or indirectly, that are currently employed are limited to infrared and ionization spectroscopy and to mass spectrometry. Principle variations of these techniques are now discussed.

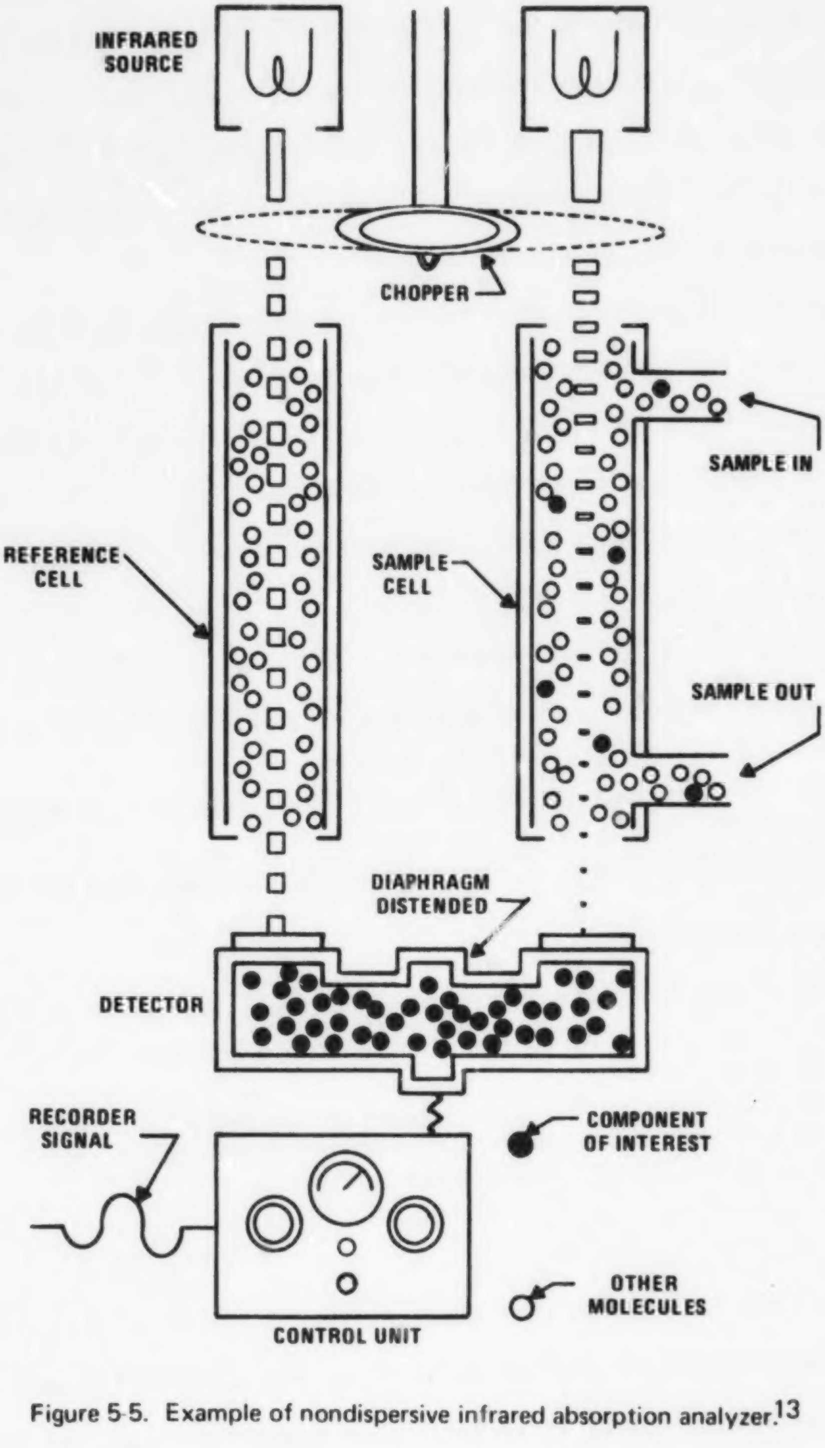
INFRARED SOURCE
CHOPPER
REFERENCE CELL
SAMPLE CELL
SAMPLE IN
SAMPLE OUT
DIAPHRAGM DISTENDED
DETECTOR
RECORDER SIGNAL
COMPONENT OF INTEREST
OTHER MOLECULES
CONTROL UNIT

Figure 5-5. Example of nondispersive infrared absorption analyzer.[13]

Nondispersive Infrared Absorption (NDIR) - This procedure, the only type of infrared analysis that has had much application in this field, is described in a recent survey of hydrocarbon methodology as follows:[13]

> Nondispersive infrared spectometry is a technique based upon the broadband absorption characterisitics of certain gases in the wavelength region of a few micrometers. Infrared radiation is typically directed through two separate absorption cells -- a reference cell and a sample cell (see Figure 5-5). The sealed reference cell is filled with non-absorbing gas, such as nitrogen or argon. The sample cell is physically identical to the reference cell and receives a continuous stream of the gas being analyzed. When a particular hydrocarbon is present, the IR absorption is proportional to the molecular concentration of that gas. The detector consists of a double chamber separated by an impermeable diaphragm. Radiant energy passing through the two absorption cells heats the two portions of the detector chamber differentially. The pressure difference causes the diaphragm to distend and vary a capacitance which is measured electronically. The variation in capacitance is proportional to the concentration of the component of gas present. By optically chopping the IR radiation, the capacitance may be made to change periodically, and as a result, the electronic readout problems are facilitated.
>
> Beckman, Horiba, and Mine Safety Appliances all manufacture NDIR analyzers based on the above principles, and use two IR sources. Ecological Instruments used a single radiation source. Infrared Industries uses two concave mirrors, thus allowing a single source arrangement. Bendix produces an analyzer with the two detector chambers in series; both detectors are filled with the gas under measurement. The gas in the forward chamber is heated by the center of the absorption band; the gas in the rear chamber by the edges of the band. Hydrocarbon gas in the sample will absorb primarily in the center of the band and thus cause the front chamber to become cooler. The pressure change is detected as a change in capacitance and read out as previously described.
>
> NDIR instruments are usually subject to interference because other gases (e.g., H_2O, CO_2) absorb at the wavelength of the gas of interest. Efforts to eliminate the interferences by use of reference cells or optional filters are only partially successful. For HC monitoring the detector is filled with one or several different hydrocarbons, which may be different from the HC contained in the sample. This will cause a disproportionate response. Other sources of errors include such things as gas leaks in detector and reference cells, inaccurate zero and span gases, non-linear response, and drift in the electronics.

Infrared analyzers are also used to measure carbon dioxide produced by oxidation of hydrocarbons, which can then be translated into an indirect measurement of total hydrocarbons.

Flame Ionization Detection (FID) - First reported as a hydrocarbon detector by Andreatch and Feinland[14] and others[15] approximately 15 years ago, the flame ionization detector (FID) has since achieved considerable recognition. FID is also well documented in reference 13:

> With standard FID, air sample is introduced into a hydrogen flame (see Figure 5-6). The combination of even 0.1 ppm of a hydrocarbon produces measurable ionization which is a function of the number of carbon ions present. A collector surrounding the flame is made positive by an external power supply and the ion current caused by the hydrocarbons is measured electronically. Since pure hydrogen burning in air produces very little ionization, the effects of background subtraction are minimized. The output current calibrated in ppm (or percentage) is read on a panel meter or chart recorder.
>
> Hydrocarbons containing nitrogen, oxygen, or halogen atoms give a reduced response. Thus, FID hydrocarbon analyzers are almost universally calibrated in terms of a gas such as methane or hexane and the output read in ppm of carbon measured as methane or hexane.
>
> It is important to note that nitrogen, CO, and CO_2 do not produce interferences. Patterson and Henein point out that although there is a very low sensitivity to water vapor, condensed water vapor may block the sample entry tube and cause erratic readings. Also when oxygen is present in excess of 4%, a significantly lower output reading may occur. Beckman Instruments report that relative response of the Model 400 Hydrocarbon Analyzer to various hydrocarbons, including those with attached oxygen, chlorine, and nitrogen atoms in Table 5-1. The response is given in effective carbon numbers (ECN) where:
>
> $$\text{ECN} = \frac{\text{Instrument response caused by atom of given type}}{\text{Instrument response caused by aliphatic carbon atom}}$$
>
> These values are true for one mode of operation of a specific detector under specific conditions (e.g., mixed N_2, H_2 fuel). However, these numbers may vary widely for different operating conditions and for different detectors.

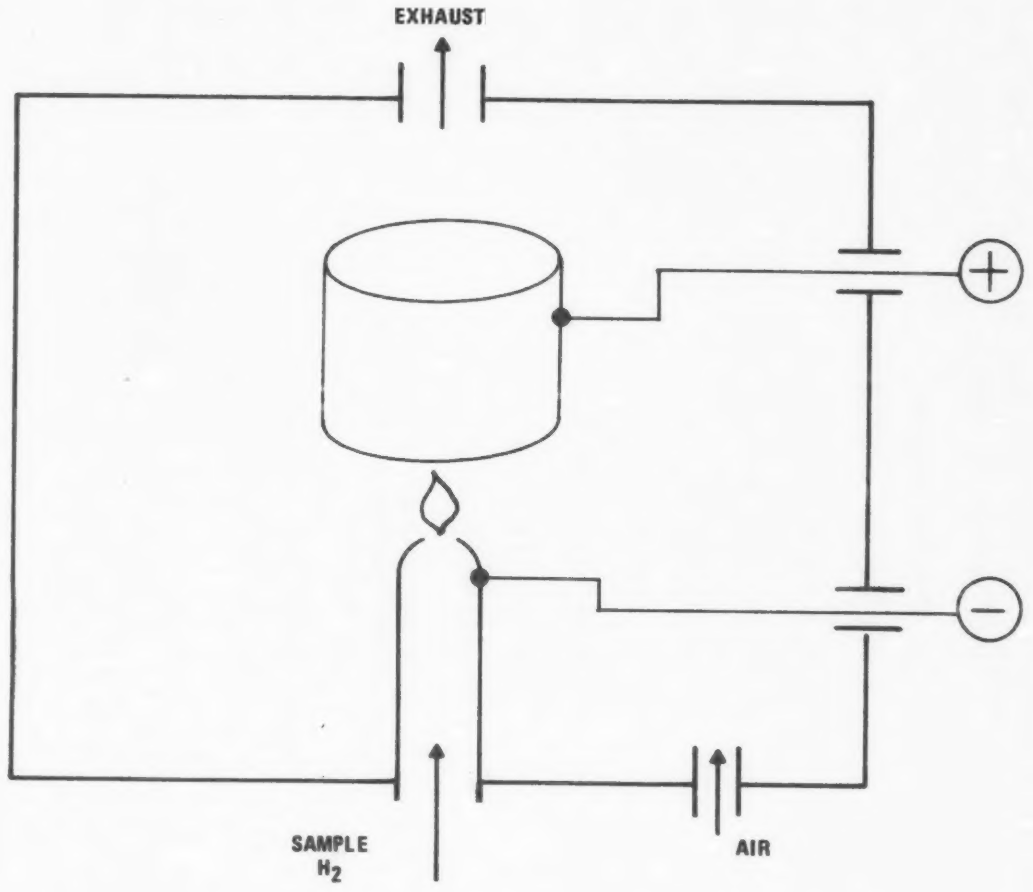
EXHAUST
+
−
SAMPLE
H_2
AIR

Figure 5-6. Flame ionization detector.[13]

Table 5.1 APPROXIMATE EFFECTIVE CARBON NUMBERS[13]

Type of atom	Occurrence	Effective carbon number
Carbon	In aliphatic compound	+1.0
Carbon	In aromatic compound	+1.0
Carbon	In olefinic compound	+0.95
Carbon	In acetylenic compound	+1.30
Carbon	In carbonyl radical	0.0
Carbon	In nitrate	+0.3
Oxygen	In ether	-1.0
Oxygen	In primary alcohol	-0.6
Oxygen	In secondary alcohol	-0.75
Oxygen	In tertiary alcohol, ester	-0.25
Chlorine	As two or more chlorine atoms on single aliphatic carbon atom	-0.12 each
Chlorine	In olefinic carbon atom	+0.05
Nitrogen	In amine	Value similar to that for oxygen atom in corresponding alcohol

Gas Chromatography (GC) - Measurement of hydrocarbons by GC is a well-documented process.[16-18] Normally thought of as a device for separating a hydrocarbon mixture into its individual compounds, GC may also be used to separate nonmethane hydrocarbons from the other gases in a sample.

Here again, reference 13 provides a well-stated description of the basic GC operation:

> Gas chromatographs have been used manually by research laboratories to monitor hydrocarbons for many years. The great power of this technique is the unique ability to separate hydrocarbons into a number of individual compounds. In principle,GC is a method for physically separating a gaseous mixture into its components by passing it through a column with a high surface-to-volume ratio (see Figure 5-7). The surface area consists of a solid material or a liquid dispersed on a solid. The segregation of the various components depends upon their selective absorption into the column material. An inert carrier gas moves the sample through the column. If the gas sample consists of different hydrocarbons, the different components will require different times to pass through the column. The weakly absorbed components are the first to emerge from the column. The selective process is highly temperature-sensitive and thus requires that most of the components of the chromatograph be housed in a temperature-controlled oven. As the various components emerge from the column, their identification and concentration are determined by an appropriate detector. For hydrocarbons, flame ionization detection, described in the previous section, is almost universally employed.

A value for total nonmethane hydrocarbons can be generated chromatographically by summing the individual concentrations as they are revealed by their respective chromatogram peaks. Another approach is to operate the chromatograph in such a manner that all nonmethane hydrocarbons elute as one from the column. One peak on the chromatogram then represents total nonmethane hydrocarbons.

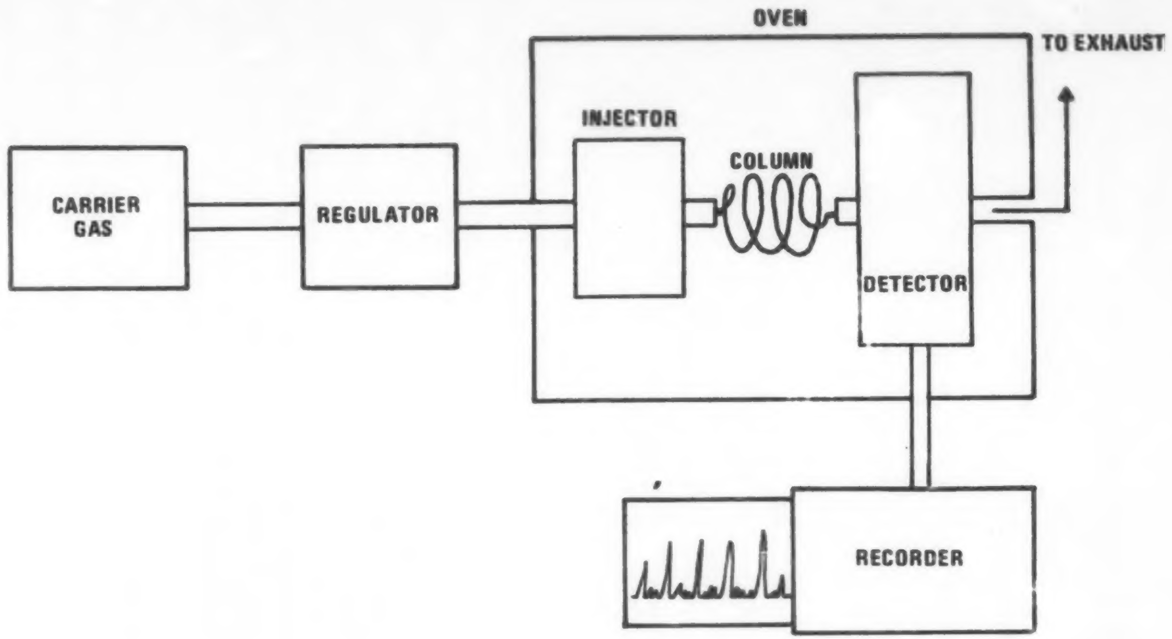
OVEN
TO EXHAUST
INJECTOR
COLUMN
CARRIER GAS
REGULATOR
DETECTOR
RECORDER

Figure 5-7. Main components of gas chromatograph.[13]

Mass Spectrometry (MS) - Mass spectrometry is described as "... essential to the absolute identification of organic components..." in a recent survey of hydrocarbon detection techniques.[19] Because individual compound identification is not an absolute requirement for the measurement of total nonmethane hydrocarbons, MS is mentioned here for the benefit of those who sample sources emitting single species of hydrocarbons for which confirmation of their presence is required.

Mass spectrometers sort a gas into its individual components by first ionizing the individual gas molecules. The ionized molecules are then subjected to various physical effects that serve to classify or resolve them into their respective mass numbers. Several types of mass spectrometers are explained by Ewing.[20] By studying the relative intensities of the mass numbers generated, a value for total methane hydrocarbons could probably be generated.

Total Combustion Analysis (TCA) - Personnel of the Los Angeles County Air Pollution Control District have reported their progress with implementation of the concept of TCA for several years.[21-24] The following quotation is taken from Solo et al.[24]

> The Los Angeles Rule 66 solvent control program has been in use for almost a decade. Measurements of source emissions for organic carbon are a vital adjunct for determining compliance with the law. The latter is accomplished using an analytical system termed Total Combustion Analysis (TCA). It involves the measurement of stack flow volume, and the collection of samples in a stainless steel freezeout trap followed by an 8-liter stainless tank in tandem. An analysis of the organic carbon in trap and tank is made by conversion and measurement of CO_2. The results are scaled to the total exhaust flow

> volume. Thus, a measurement of total organic carbon in pounds per hour is obtained, which for practical purposes is interpreted as being very close to the actual organic quantity.
>
> The detector system has historically been a non-dispersive infrared analyzer sensitized to CO_2. Recently, we have been testing a hydrogen flame ionization detector (FID) in place of the non-dispersive system. In the FID version of the TCA instrument, it is necessary to convert the CO_2 to CH_4 in order to utilize the enhanced sensitivity of the detector. This is accomplished over a nickel catalyst. Results indicate that the newer FID detector is preferable for low concentration cases, and can be used satisfactorily in any event for all measurements of organic carbon.

Figure 5-8 illustrates the analytical steps for both the cold trap and the evacuated cylinder. Other sampling devices, such as the Universal Collector, syringe, purge flask, and collapsible bag could also be used.

Because all hydrocarbons reach the FID as CH_4, the problem of varying response factors, as explained earlier, is eliminated.

Corrosive gases created by combustion of halogenated hydrocarbon could create problems for this system. A possible remedy would be to install a selective absorber for these gases between the oxidizer and the reducing catalyst.

No commercial, fieldproven TCA's are presently available. If a semiportable version can be developed, this approach will become even more appealing, because the direct sample technique can then be used. Substitutions of an FID in place of the NDIR greatly enhances the analysis system's sensitivity.

5.6 Conclusion

This section has dealt with the determination of total nonmethane hydrocarbon emissions through emission measurements. In the course of describing various sampling and analytical techniques that are currently available,

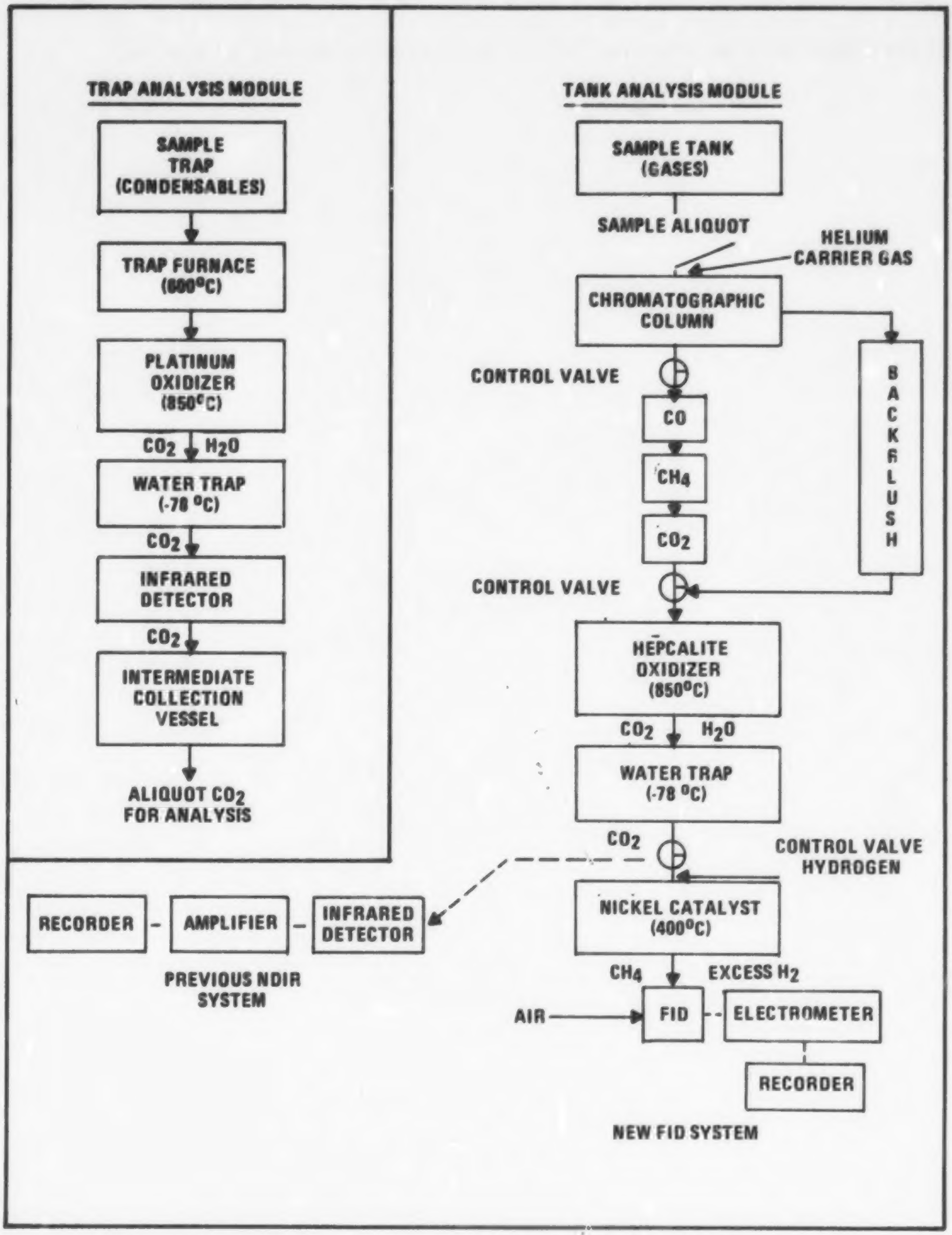
TRAP ANALYSIS MODULE
SAMPLE TRAP (CONDENSABLES)
TRAP FURNACE (600°C)
PLATINUM OXIDIZER (850°C)
CO2
H2O
WATER TRAP (-78 °C)
CO2
INFRARED DETECTOR
CO2
INTERMEDIATE COLLECTION VESSEL
ALIQUOT CO2 FOR ANALYSIS
TANK ANALYSIS MODULE
SAMPLE TANK (GASES)
SAMPLE ALIQUOT
HELIUM CARRIER GAS
CHROMATOGRAPHIC COLUMN
CONTROL VALVE
CO
CH4
CO2
BACKFLUSH
CONTROL VALVE
HEPCALITE OXIDIZER (850°C)
CO2
H2O
WATER TRAP (-78 °C)
CO2
CONTROL VALVE
HYDROGEN
NICKEL CATALYST (400°C)
CH4
EXCESS H2
AIR
FID
ELECTROMETER
RECORDER
NEW FID SYSTEM
RECORDER
AMPLIFIER
INFRARED DETECTOR
PREVIOUS NDIR SYSTEM

Figure 5-8. Block flow diagram of TCA trap and tank analysis systems showing difference between NDIR and ID detection.[24]

concepts have been presented that should orient those persons responsible for determining source compliance with emission standards to the type of questions that must be resolved before a particular method is applied.

5.7 REFERENCES FOR CHAPTER 5

1. Air pollution. 2nd Ed., Vol. II. Stern, A.C. (ed.). New York, Academic Press, 1968. p.3-54.

2. Sampling Atmospheres for Analysis of Gases and Vapors. American Society for Testing and Materials, Philadelphia, Pa., DI605 ASTM Annual Standards. Part 26, 1974. p. 285-306.

3. Sampling and Storage of Gases and Vapors, Methods of Air Sampling and Analysis. Part 1. Intersociety Committee of American Public Health Association, Washington, D.C. 1972 p. 43-55

4. Title 40 - Protection of Environment. Test Methods 1-4. Federal Register. 36 (247): 24882-24887, December 23, 1971.

5. Air Sampling Instruments. 4th Edition American Conference of Governmental and Industrial Hygienists, Sections A and B. 1972.

6. White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel. A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere. Amer. Ind. Hyg. Assoc. J. 31(2): 225, March - April 1970.

7. Mueller, F.X., and J.A. Miller. Determination of Organic Vapors in Industrial Atmospheres. Amer. Lab. 6(5): 49-61, May 1974.

8. Isbell, A.F., Jr. Development of Selective Hydrocarbon Sampling System and Field Evaluation with Conventional Analytical System. U.S. Environmental Protection Agency, Research Triangle Park, N.C. under Contract No. 68-02-1201. Publication No. 650/2-75-050. August 1975.

9. Gadomski, R.R., A.V. Gimbrone, M.P. David, and W.J. Green. Evaluations of Emissions and Control Technologies in the Graphic Arts Industries. Phase II: Web Offset and Metal Decorating Processes. Graphic Arts Technical Foundation, Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C. under Contract No. 68-02-001. Publication No. APTD-1463. May 1973.

10. Hales, J.M., and N.S. Laulainen. Report on Verification of Halogenated Hydrocarbon Testing and Monitoring Methodology. Battelle-Northwest, Richland, Washington. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C. under Contract No. 68-02-1409 (Task 15). 1975.

11. Title 40 - Protection of Environment. EPA Method 106 - Determination of Vinyl Chloride from Stationary Sources. Federal Register-40(248): 59550, December 24, 1975.

12. Schuetzle, D., T. J. Prater, and S. R. Ruddell. Sampling and Analysis of Emissions from Stationary Sources 1. Odor and Total Hydrocarbons. J. Air Pollution Control Assoc. 25(9): 925-32, September 1975.

13. Air - Hydrocarbon Monitoring Instrumentation. Lawrence Berkeley Laboratory, University of California, Berkeley, California. November 1973.

14. Andreatch, A.J. and R. Feinland. Continuous Trace Hydrocarbon Analysis by Flame Ionization. Anal. Chem. 32(8): 1021-1024, July 1960.

15. Morris, R.A., and R. L. Chapman. Flame Ionization Hydrocarbon Analyzer. J. Air Pollution Control Assoc. 11(10): 467-469. October 1961.

16. McNair, H.M., and E. J. Bonelli. Basic Gas Chromatography. Varian Aerograph, Inc., Walnut Hills, California. 1969.

17. Total Hydrocarbons by GC-FID. In: Methods Of Air Sampling and Analysis. Intersociety Committee of American Public Health Association, Washington, D.C. ISC 41301-02 71T. 1972

18. Jeltes, R. and E. Burghardt. Automatic Gas Chromatographic Measurement of C_1 - C_5 Hydrocarbons in Air. Atmos. Environ. 6: 793-805, 1972.

19. Survey of Methods for Measuring Total Hydrocarbons. DeBell and Richardson, Inc., Enfield, Conn. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C., under Contract No. 68-02-2075. 1976.

20. Ewing, G.W. Instrumental Methods of Chemical Analysis. New York, McGraw-Hill Book Company, 1969.

21. MacPhee, R. D., and M. Karamoto. Recommended Test Methods for Organic Solvents and Vapors (Rule 66). Air Pollution Control District, County of Los Angeles, Los Angeles, California. April 1968.

22. DeVorkin,H.Sampling for Compliance with Rule 66. (Presented at 62nd Annual Meeting of Air Pollution Control Association. New York. Paper No. 69-49. June 22-26, 1969.)

23. Salo, A.E., W. L. Oaks, and D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. (Presented at 67th Annual Meeting of Air Pollution Control Assoc. Denver. Paper No. 74-190. June 9-13, 1974.)

24. Salo, A.E., S. Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. (Presented at 68th Annual Meeting of the Air Pollution Control Association. Boston. Paper No. 75-33.2 June 15-20, 1975.)

25. Neal, R.C., P. L. Hayden. D.R. Grove and E.A. Brackbill. Test Methods for the Evaluation of Organic Emissions. (Presented at 1st Annual Conference of Source Evaluation Society. Dayton. September 17-19, 1975.)

26. Woods, J. and R. Melcher. Review of Analytical Methods and Techniques - (Study to Support New Source Performance Standards for Industrial Degreasing Operations). Dow Chemical Co., Freeport, Texas - Prepared for U.S. Environmental Protection Agency, Research Triangle Park, N.C.,under Contract No. 68-02-1329. (Sub Task 2) 1975.